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THE ELECTRICAL CONDUCTIVITY OF LIQUID AMMONIA SOLUTIONS.

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In a recent paper[1] the authors pointed out some analogies between the properties of liquid ammonia and those of water, showing, among other things, that of all known electrolytic solvents ammonia most closely approaches water in its power of forming solutions which conduct the electric current. The interest which attaches to the study of liquids with such high conducting power has led the authors to undertake more careful measurements of the conductivity of ammonia solutions than have yet been attempted.

None of the measurements hitherto made on ammonia solutions[2] can be used for more than a qualitative comparison with aqueous and other solutions; and from somewhat extended experiments on the part of the authors it became evident that reliable quantitative results were not to be obtained with any of the simple forms of apparatus used in previous investigations. It was therefore found necessary to devise a form of apparatus by means of which the solvent could be purified and isolated for a considerable length of time. It was also essential to arrange the apparatus so that both solvent and solute could be added safely and conveniently. At the

1 This JOURNAL, **21**, 8 (1899).

2 Cady: J. phys. Chem., **1**, 707 (1897); and Goodwin and Thompson: Phys. Rev., **8**, 38 (1899).

same time it was necessary to be able to remove known portions of the solution from the resistance vessel, and to supply the place of the removed solution by fresh solvent. Finally the escape of large quantities of gaseous ammonia into the air of the laboratory had to be avoided.

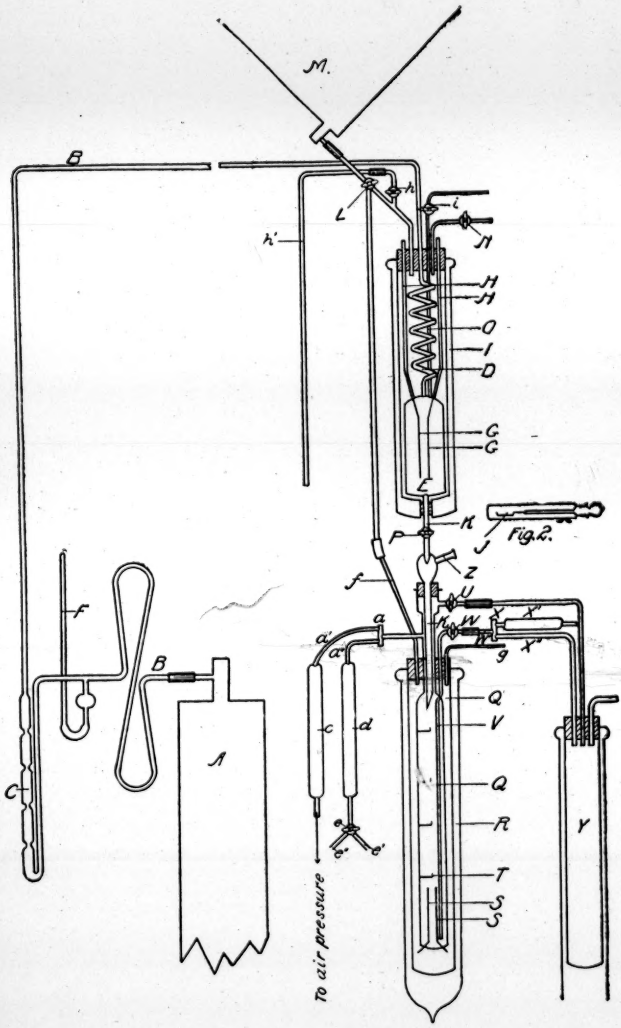
The following is a description of the form of apparatus which the authors found to be well adapted to meet the above enumerated requirements.

Description of the Apparatus.

The steel cylinder *A*, containing the liquid ammonia which is to be purified, is provided with a valve of a pattern which permits the easy regulation of the flow of gas. The metal delivery tube of the valve was connected with the glass tube *B* by means of a piece of rubber tubing, which, to withstand the pressure, was first tightly tied and then wrapped with tape.

On opening the valve the gas passes from the cylinder *A* through the glass tube *B*, which carries an asbestos filter, *C*, into the condensing spiral *D*, whence it runs as a liquid into the receptacle *E*. To the tube *B* is attached a pressure gauge *F*, for the purpose of assisting the manipulator to regulate more easily the flow of gas. The asbestos filter is a glass tube filled with carefully dried asbestos. The constrictions are for the purpose of preventing the packing of the asbestos into one end of the tube when the pressure from *A* is turned on. The asbestos used was the serpentine variety which, unless freed of its water of crystallization by long heating over the blast-lamp, continued indefinitely to give up sufficient moisture to the ammonia to affect materially its conductivity.

The filter is an important part of the purifying apparatus, its object being to retain minute particles of solid material which may be carried over by the stream of gas. That foreign matter was carried over from the stock cylinder is proved by the following observations: Other conditions being the same it was not possible without the filter to obtain a distillate with anything like the high resistance of the pure solvent. With fresh sodium in the cylinder *A*, a sufficient quantity of the metal was carried over to give the ammonia in the receptacle *E*, a decided blue color, and to reduce the resistance in


M.
B
h'
L
h
i
N
H
H
O
I
D
G
G
E
K
P
J
Fig.2.
Z
U
W
Y
X'
X
g
f
a
a'
B
A
C
c
d
b
b'
b''
To air pressure
Q
V
Q
R
T
S
S
Y

this cell to less than a hundredth of its value under other conditions.

The purity of the solvent was determined by making measurements of its conductivity, for which purpose a pair of electrodes, *GG*, was sealed into the receiver *E*. The electrodes are in metallic connection with the exterior and the measuring apparatus through the glass tubes *HH*, sealed around the connecting wires and filled with mercury. The receptacle and spiral were kept cold by surrounding them with a bath of liquid ammonia contained in the vacuum-jacketed vessel *I*. During the investigations this vessel developed a crack, and, the necessary tubing not being at hand to replace it, an air jacket was substituted in its stead with satisfactory results. A little alcohol between the walls of the air jacket served to absorb the moisture which otherwise would have frozen on the walls and obscured the view of the receptacle and its contents. The opening in the lower end of the vessel *I* is closed by a rubber stopper through which passes the delivery tube *K* from the receiver *E*. Care had to be taken to have this stopper fit well, as otherwise a little pressure is liable to force out liquid ammonia, which almost inevitably breaks the jacket. The upper end of the vessel, *I*, is likewise closed with a rubber stopper, which is fitted with holes, first, for the tube *L* through which ammonia is drawn from the stock cylinder *M* into the bath *I*; second, for the escape tube *N*, for carrying off the gas; and third, for the tube *O*, through which the bath may be emptied of its contents by simply closing the stop-cock *N*. Besides these, the tubes *HH*, making connection with the electrodes, also pass through this stopper. The tubes *B*, *L*, *N*, and *O* are fitted gas-tight into the stopper, while for the tubes *HH* large holes were made so that the stopper might be forced tightly into place without danger of breaking these tubes loose from their connections with the receiver *E*. When all the tubes were in place, the stopper was tied firmly to the vessel *I*, and the space around the tubes *HH* was filled up with laboratory wax.

The condensation of the gas in the spiral *D* and the receiver *E* is produced at the expense of an equivalent quantity of liquid ammonia which evaporates from the bath *I*. The

gas escapes through the tube N and is thence conducted into a carboy containing water where it is recovered as aqua ammonia.

When a sufficient quantity of liquid has been collected in the receiver E, the stop-cock P is opened and the ammonia runs into the conductivity vessel Q. This vessel is provided with a pair of electrodes, SS, which is connected with the exterior and the measuring apparatus by means of glass tubes filled with mercury in the same manner as are the electrodes GG in the upper receptacle. Connections for the electrodes SS are not shown in the figure. Five fine glass pointers, T, were sealed into the resistance cell Q, point upwards. The volume of the cell up to these different points was determined by filling with water at 25° until the respective points were just breaking the surface, and caculating the observed volumes to the volume at the boiling-point of ammonia. Sealed into the cell Q at Q' and reaching to the bottom, is a glass tube, V, which has capillary dimensions from the point at which it enters the resistance vessel to its lower end. This tube is provided with a stop-cock, W, just beyond which connection is made with the tube W'. W' carries a two-way stop-cock X. One way leads to the open air through the soda-lime drying tube X', while the other, X'', leads to the vacuum-jacketed tube Y. The purpose of this vessel Y will appear below.

The tube KK' leading from the receiver E to the vessel Q reaches well through the neck of the latter into which it is fitted by means of a rubber stopper. A short distance above this stopper the tube K is enlarged and the tube from above is sealed in so that it projects about 1 centimeter within the enlargement, as shown in the figure. In the side of the enlargement, and with an upward slant, is sealed a tube, Z, through which the solute is introduced into the conductivity cell.

The solute is weighed out in a small platinum spoon, J, enclosed in a weighing tube as shown in Figure 2. In order to introduce the solute, the spoon is removed from the weighing tube and placed in position in the tube Z. A half turn on the axis of the spoon holder empties the contents into the

cell Q. Any portions of the solute which may remain clinging to the spoon or to the side of the tube are washed down by the ammonia drawn from the receiver E.

Just below the stopper, through which K' enters the neck of the resistance receptacle, is sealed a tube provided with a stop-cock, U, and leading to the vessel Y. This attachment enables the operator to wash out the neck of the vessel Q as described below.

To the neck of the vessel Q is sealed a second tube carrying a two-way stop-cock, a, one branch of which, a', leads through the phosphorus pentoxide drying tube c to the pressure reservoir containing dry air free from carbon dioxide. The other branch, a'', leads through a soda-lime drying-tube, d, to a two-way stop-cock, e, one branch, e', of which opens to the air, while the other, e'', leads to a collecting bottle containing water.

Preparatory to making a series of measurements, the resistance vessel Q must be well washed out and supplied with pure solvent from the receptacle E. To accomplish this, ammonia is drawn down by opening the stop-cock P until the electrodes SS are well covered, the stop-cocks a and e having previously been set to open the way through a'' and e'', and the stop-cocks W and U having been closed. By this arrangement of the stop-cocks the ammonia vapor escapes through e'' into the absorption bottle. The stop-cocks W and X, through X'', are then opened, and a is set to close a'' and open a'. The pressure from the air reservoir on the surface of the liquid forces this latter out through the tube V into the vessel Y, thus emptying Q. After emptying the resistance cell the stop-cocks are turned back to their original positions and a fresh quantity of ammonia is drawn down into the cell. This operation is repeated until tests of the resistance in the cell Q show that all soluble material has been removed. U is then opened, and with W and a closed, the liquid is run down into the lower vessel until it fills the cell completely and runs over into Y through U. The stopper is then removed from Z and a quantity of ammonia is allowed to blow out through this portion of the apparatus. The ammonia is then run out through V in the manner described above. In this way the

resistance cell is thoroughly washed. The next lot of ammonia run down is tested, and in case its resistance indicates sufficient washing of the cell Q the operator proceeds to the addition of the solute.

The previously weighed solute is introduced in the manner described above, and, with the stop-cocks properly set, ammonia is let down into the resistance cell until the first pointer is slightly more than covered. The stop-cock e is then set to open the way through e' to the outside air; W is opened, and X is set to open the way through X''. With this arrangement of the stop-cocks, the back pressure from the vessel Y forces ammonia vapor through the liquid in the resistance cell. This current of ammonia gas, warmed by its passage through X'', W, and V, evaporates ammonia from the resistance cell and at the same time thoroughly mixes the solution. After passing the vapor for a few moments, X'' is closed and X' is opened. Both the tubes V and e' being, with this arrangement of the stop-cocks, open to the air, the liquid in Q and V comes into pressure equilibrium. If, after this operation, the tip of the glass pointer is not visible just breaking through the surface of the solution, the above-described operation is repeated until the point just touches the surface. The resistance is then measured. The solution is then diluted, stirred, adjusted to the next pointer, and the resistance again read. This operation is repeated until the last point is reached, after which the solution is forced out through the tube V in the manner described above, until the lowest point is reached, when the stop-cock W is closed. This leaves a known quantity of solute in the resistance cell. More solvent is then added, the volume adjusted to the second pointer, and the resistance again measured. In this manner measurements may be made on solutions carried to any desired degree of dilution.

The Constant Temperature Bath.—In order to maintain the resistance vessel Q at a constant temperature it is immersed in a bath of liquid ammonia contained in the Dewar tube R. To overcome the considerable superheating which ammonia exhibits in glass vessels, it was at first attempted to boil the liquid in the bath by means of a spiral of platinum wire

heated by a current of electricity. This plan was soon abandoned, however, for the much simpler and quite as efficient method of placing blackened platinum tetrahedra in the bottom of the bath and warming them by the radiations from an ordinary incandescent lamp. No errors from changes in the temperature of the bath could be observed.

The mouth of the vessel *R* is fitted with a rubber stopper which supports the resistance cell *Q*, and in which provision is made for the mercury connecting tubes, and for the tubes *f* and *g* for introducing the liquid and carrying off the gas, respectively. The mercury connecting tubes are not shown in the figure. Liquid ammonia is introduced into the bath *R* by opening the stop-cock *L* through *f* and then opening the valve on the steel cylinder *M*.

Recovery of Liquid Ammonia from Receptacle Y.—A glass tube carrying a stop-cock, *h*, is sealed to the tube *L*, through which ammonia is drawn from the stock cylinder to the baths *I* and *R*. If this stop-cock is opened and an aspirator attached to the exit tube *N*, then liquid from without may be drawn into the bath *I* by connecting a tube *h'* to *h*, and immersing the end of the former in the liquid. Thus, ammonia which has been used in the resistance cell can be drawn from the vessel *Y* into the bath *I* and utilized for cooling the receiver.

To Empty the Condensing Bath, I.—After considerable liquid has been evaporated from the bath *I*, the residue becomes so impure that the frothing of the liquid in boiling interferes with the distillation. By opening the stop-cock *i* on the tube *O*, and closing the stop-cock on the exit tube *N*, the pressure of the boiling ammonia forces out the liquid through *O*, thus emptying the bath of its contents. This was always necessary at the end of a series of experiments.

The apparatus is somewhat complicated, but after a little practice on the part of the operators, measurements can be carried out easily and with a fair degree of accuracy. With everything in order, from two to three series of measurements can be made in half a day.

The Solvent.—The ammonia used in these experiments was the "Liquid Anhydrous Ammonia" of commerce, such as is

used for refrigerating purposes. An earlier plan, of distilling the ammonia once or twice before its final distillation from the cylinder A of the purifying apparatus, was later abandoned for the simpler and entirely satisfactory plan of drawing the liquid from the stock cylinder directly into the smaller cylinder, into which latter a quantity of metallic sodium had previously been introduced. The sodium dissolves in the ammonia, and any water present in solution is at once acted upon by the metal with the formation of insoluble sodium hydroxide. The sodium not used up by the water present reacts slowly with the ammonia to form sodamide and hydrogen. The sodamide is somewhat soluble and is an efficient drying agent. The ammonia distilled from sodamide into the receptacle E was very pure, as was shown by tests of its resistance, which, after the introduction of a good asbestos filter in the train, was found to be uniformly very high. In fact, the resistance was so great that it was not possible to measure it, even approximately, with the measuring apparatus in its present form, and, moreover, the high resistance did not diminish when the liquid remained in the cell for some hours, proving that, contrary to the behavior of water, liquid ammonia is without appreciable action on glass. Attempts to obtain the purest possible ammonia in the receiver E were not made, partly for the reason that the means were not at hand for measuring very high resistances, but principally for the reason that other sources of impurity were present which could not be overcome in the present experiments.

While ammonia of a specific conductivity below 0.01×10^{-6} was easily obtained in the receiver, it was not possible to produce a liquid which, after being run into the resistance cell Q, showed a specific conductivity lower than about 0.10×10^{-6}.[1]

Certainly one of the sources of impurity, to which reference has just been made, is moisture which enters the stop-cock P. Water lowers the resistance of liquid ammonia. As a result of the contact of cold ammonia with the stop-cock, moisture condenses on the latter, and small, but sufficient, quantities work in around it to reduce the resistance of the solvent very

[1] Goodwin and Thompson [Phys. Rev., 8, 47 (1899)] give 1.6×10^{-4} as the mean specific conductivity of liquid ammonia at temperatures between $-30°$ and $-12°$, a value very much greater than the minimum obtained in these experiments.

materially. Nor is this defect easily remedied. An ordinary glass stop-cock cannot be ground to be absolutely tight without the use of lubricant, which must, of course, be omitted from a cock used for the present purpose. After experimenting with a number of different styles of stop-cocks, a mercury-seal cock was finally used for the measurements recorded in this paper. The mercury, however, was left out and the empty spaces on either end of the key opened into the air through pieces of small rubber tubing of considerable length. The ammonia which leaked through the stop-cock was thus allowed to escape, while the deposition of moisture was confined to the exterior of the stop-cock. Even with this stop-cock, which gave much better results than any other form used, the specific conductivity of the solvent in the resistance cell Q could not be reduced much below 0.10×10^{-6}. The specific conductivity varied between 0.10×10^{-6} and 0.15×10^{-6}, or even more, and could not be accurately controlled.

Solutes.—With the exception of sodamide, all the salts and other substances used in these experiments were carefully purified and thoroughly dried before being used. The concentration of the sodamide solutions for which measurements are given were arrived at by calculation from a weighed quantity of sodium added to the solvent.

Measuring Apparatus, Constants, and Units.—The bridge and telephone method of Kohlrausch was used in making the measurements of conductivity recorded in this paper. With the highest dilutions the resistance reached 20,000 ohms. At this resistance the telephone minimum became so poor that it was not practicable with the present form of the apparatus to carry the dilutions higher. Besides the errors introduced by the variable conductivity of the solvent, some of the inaccuracies in the measurements at high dilutions are to be attributed to the difficulty of accurately setting the bridge at such high resistances. Another source of error which is easily introduced is insufficient stirring. The solutions were usually stirred until no further change could be detected in the conductivity, but doubtless some errors are due to this cause.

The units recently introduced by Kohlrausch[1] were used in calculating the values given below.

The resistance capacity of the cell, determined by means of a fiftieth-normal solution of potassium chloride of specific conductivity 0.002397[2] at 18°, was 0.07344.

The volumes of the conductivity cell at the boiling-point of ammonia for the five points was 45.70 cc., 67.67 cc., 94.75 cc., 117.09 cc., and 141.16 cc., respectively. The volume to the first point plus the volume of the stirring tube V was 46.62 cc.

The atomic weights recently recommended by the committee of the German Chemical Society, which are calculated on the basis of oxygen = 16, were used.

The correction made for the conductivity of the solvent was 0.13×10^{-6}, which was approximately the mean conductivity of the solvent as measured in the resistance cell Q, after thoroughly washing out the latter. The correction for the highest dilutions amounts to about 4 per cent.

Numerical Results.—In the following tables are given the results of measurements on twenty-five different substances. Besides these substances measurements were also made on potassium iodide, sodium nitrate, ammonium bromide, and silver nitrate, but because of the uncertain value of the resistance capacity of the cell at the time of making these measurements, they are not included in the tables below.

The dilutions, expressed in liters per gram molecule, are denoted by v, the molecular conductivities by μ_v, which correspond respectively to $\varphi 10^{-8}$ and Δ in Kohlrausch's[3] notation.

[1] Kohlrausch und Holborn: Das Leitvermögen der Electrolyte, p. 1 (1899); Kohlrausch, Holborn, und Diesselhorst: Wied. Ann., **64**, 417 (1898).

[2] Kohlrausch: *Loc. cit.*

[3] *Ibid.*

Table I—Potassium Bromide.

v.	μ_v.	v.	μ_v.
301.9	210.6	7093.0	324.6
447.0	228.3	8553.0	323.9
625.9	242.3	12410.0	329.7
773.4	251.7	17380.0	333.5
932.6	259.5	21480.0	336.1
1354.0	272.9	25900.0	337.0
1895.0	286.8	37590.0	338.7
2343.0	293.7	52640.0	339.6
2824.0	299.8	65040.0	340.2
4099.0	308.5	78430.0	340.4
5740.0	317.6		

Table II—Potassium Nitrate.

v.	μ_v.	v.	μ_v.
324.0	192.7	7614.0	314.9
479.9	210.1	9181.0	318.8
671.9	226.0	13330.0	322.1
830.2	236.7	18660.0	327.9
1001.0	245.0	23060.0	330.1
1453.0	261.7	27800.0	331.4
2082.0	274.9	40360.0	333.7
2514.0	282.9	56510.0	337.4
3032.0	289.3	69820.0	338.6
4401.0	301.4	84200.0	337.6
6162.0	309.9		

Table III—Potassium Metanitrobenzenesulphonate.

v.	μ_v.	v.	μ_v.
144.8	135.5	4522.0	242.8
214.5	147.2	6332.0	250.9
371.1	166.8	9190.0	257.3
538.7	179.8	12870.0	263.0
754.3	192.5	18680.0	268.6
1095.0	204.1	26150.0	271.0
1533.0	215.5	37960.0	276.1
2225.0	225.8	53160.0	281.2
3116.0	234.5		

Table IV—Sodium Bromide.

v.	μ_v.	v.	μ_v.
287.0	200.0	6744.0	287.7
425.0	214.5	8132.0	289.9
595.1	227.4	11810.0	292.0
735.4	234.7	16530.0	296.0
886.8	240.2	20420.0	297.9
1287.0	251.7	24630.0	298.2
1802.0	262.5	35750.0	298.1
2227.0	266.8	50050.0	299.8
2686.0	271.1	61840.0	303.0
3898.0	277.6	74580.0	302.1
5458.0	283.8		

Table V—Sodium Bromate.

v.	μ_v.	v.	μ_v.
342.3	179.4	1535.0	229.5
506.9	193.4	2150.0	238.6
709.8	205.1	2656.0	244.0
877.0	212.5	3203.0	247.8
1058.0	218.7	4648.0	255.2

Table VI—Sodium Bromate.

v.	μ_v.	v.	μ_v.
323.4	177.6	7600.0	263.7
479.0	191.5	9164.0	265.9
670.7	210.8	13300.0	269.1
828.7	211.0	18620.0	271.1
999.3	217.1	23020.0	273.4
1451.0	227.9	27760.0	273.9
2031.0	238.0	40280.0	275.1
2509.0	243.1	56400.0	275.8
3026.0	247.5	69690.0	276.7
4392.0	253.9	84040.0	275.7
6150.0	260.9		

Table VII—Ammonium Chloride.

v.	μ_v.	v.	μ_v.
298.9	159.0	7023.0	280.5
442.6	176.3	8468.0	285.6
619.8	191.2	12290.0	292.0
765.8	200.3	17210.0	296.2
923.4	208.7	21270.0	298.8
1340.0	224.4	25650.0	301.1
1877.0	238.9	37220.0	303.7
2319.0	246.5	52120.0	303.9
2796.0	253.1	64400.0	301.4
4059.0	264.7	77660.0	304.4
5684.0	274.2		

Table VIII—Ammonium Nitrate.

v.	μ_v.	v.	μ_v.
105.1	169.7	6057.0	286.6
155.8	183.8	7385.0	288.9
218.1	195.3	9024.0	291.4
269.5	203.1	13100.0	294.2
324.9	210.4	18340.0	296.3
471.6	222.4	22660.0	296.6
660.4	233.7	27330.0	297.0
816.0	240.5	39670.0	297.1
984.0	245.6	55540.0	295.5
1428.0	256.9	68640.0	298.5
2000.0	266.8	82760.0	298.7
2471.0	271.1	120100.0	294.3
2980.0	276.1	168200.0	299.4
4325.0	281.4		

Table IX—Silver Iodide.

v.	μ_v.	v.	μ_v.
212.1	71.06	4984.0	198.1
314.1	83.50	6011.0	205.9
439.8	96.29	8724.0	221.1
543.5	100.9	12210.0	233.9
655.4	107.9	15100.0	242.1
951.3	122.7	18200.0	247.5
1332.0	137.1	26420.0	256.3
1646.0	146.5	36990.0	265.2
1985.0	155.5	45710.0	270.6
2881.0	175.2	55120.0	274.0
4034.0	188.2	80000.0	276.0

Table X—Silver Cyanide.

v.	μ_v.	v.	μ_v.
44.77	20.21	556.6	21.52
66.30	20.53	779.4	21.65
92.84	20.78	1131.0	21.54
134.84	20.88	1584.0	21.65
188.7	21.17	2299.0	21.45
273.8	21.31	3219.0	21.50
383.4	20.64		

Table XI—Mercuric Cyanide.

v.	μ_v.	v.	μ_v.
24.17	1.20	6.92	1.44
35.79	1.18	10.25	1.35
50.12	1.17	14.35	1.30
72.75	1.16	20.83	1.25
101.9	1.16	29.17	1.23
147.9	1.16	42.34	1.23
207.1	1.17	59.28	1.22
		86.04	1.20
		120.5	1.20
		174.9	1.19
		244.9	1.19

Table XII—Metadinitrobenzene.

v.	μ_v.	v.	μ_v.
354.5	131.6	5590.0	217.0
525.0	144.1	8114.0	221.3
735.0	155.7	11360.0	(225.8)
1067.0	168.6	14040.0	232.5
1494.0	178.7	20380.0	234.3
2226.0	190.4	29570.0	236.0
3231.0	203.7		

Table XIII—Strontium Nitrate.

v.	μ_v.	v.	μ_v.
286.2	145.0	8108.0	299.0
423.9	160.2	11770.0	321.5
593.3	173.7	16480.0	344.4
733.2	182.6	20360.0	359.3
884.1	190.6	24550.0	371.1
1283.0	207.0	35640.0	403.4
1797.0	221.9	49900.0	431.4
2220.0	232.1	61660.0	449.0
2677.0	240.8	74350.0	466.2
3886.0	258.1	107900.0	491.9
5441.0	275.8	151100.0	514.2
6724.0	288.4		

Table XIV—Sodamide.

v.	μ_v.	v.	μ_v.
27.49	4.923	169.2	15.69
38.49	6.013	236.9	19.53
47.56	6.896	343.8	23.84
57.35	7.739	481.4	28.17
83.23	9.698	698.7	32.35
116.5	12.09	978.6	35.52

Table XV—Acetamide.

v.	μ_v.	v.	μ_v.
5.020	0.2841	30.71	0.4507
9.434	0.3134	43.00	0.4850
10.41	0.3413	62.41	0.5266
15.11	0.3768	87.39	0.5670
21.15	0.4130		

Table XVI—Benzenesulphonamide.

v.	μ_v.	v.	μ_v.
42.00	18.03	731.0	58.43
62.19	21.70	1061.0	67.25
87.08	24.41	1485.0	76.72
126.4	28.45	2156.0	87.86
177.0	32.65	3019.0	106.9
256.9	38.01	4382.0	122.4
359.7	43.62	6136.0	137.2
522.0	51.05	8916.0	151.9

Table XVII—Orthomethoxybenzenesulphonamide.

v.	μ_v.	v.	μ_v.
101.2	14.13	2811.0	59.09
141.8	16.34	3937.0	67.67
175.2	17.92	4864.0	73.16
211.2	19.44	5866.0	79.36
306.6	22.88	8514.0	90.24
429.3	26.53	11920.0	101.1
530.4	29.10	14730.0	108.3
639.6	31.61	17760.0	115.7
928.3	37.33	25780.0	127.6
1300.0	42.88	36100.0	139.7
1606.0	46.79	44610.0	147.7
1937.0	51.05		

Table XVIII—Metamethoxybenzenesulphonamide.

v.	μ_v.	v.	μ_v.
57.96	23.92	1809.0	91.03
85.82	27.85	2533.0	102.2
148.5	34.71	3677.0	114.9
215.5	40.81	5149.0	124.5
301.7	45.93	7473.0	140.9
438.0	53.57	10460.0	153.5
613.3	60.91	15190.0	165.9
890.2	70.20	26280.0	183.2
1247.0	79.60		

Table XIX—Paramethoxybenzenesulphonamide.

v.	μ_v.	v.	μ_v.
55.50	11.27	1326.0	47.16
77.70	13.23	1924.0	54.93
122.8	15.51	2694.0	63.20
157.9	17.96	3910.0	73.55
229.2	21.05	5475.0	83.71
320.9	25.13	7947.0	96.01
465.8	30.01	11130.0	109.4
652.2	34.74	16150.0	126.1
946.7	40.92	22620.0	140.2

Table XX—Metanitrobenzenesulphonamide.

v.	μ_v.	v.	μ_v.
85.68	89.54	2164.0	184.6
126.9	99.70	3031.0	193.3
177.6	109.1	4399.0	200.9
257.9	119.7	6159.0	207.3
361.0	130.4	8940.0	213.9
524.0	142.0	12520.0	219.6
733.8	153.3	18170.0	222.7
1065.0	164.3	25440.0	224.1
1491.0	174.8	36930.0	227.1

Table XXI—Benzoic Sulphinide.

v.	μ_v.	v.	μ_v.
118.1	85.98	2983.0	167.5
174.8	94.45	4177.0	176.3
244.8	101.7	6062.0	184.0
355.3	110.5	8488.0	191.8
497.6	119.0	12320.0	196.6
722.1	129.3	17250.0	203.8
1011.0	139.5	25040.0	207.3
1468.0	149.6	35060.0	211.4
2055.0	159.2		

Table XXII—Trinitrotoluene.

v.	μ_v.	v.	μ_v.
158.0	164.4	2427.0	203.1
233.9	170.4	3398.0	208.0
404.8	178.0	4932.0	212.8
587.5	180.4?	10030.0	223.9
822.7	187.5	14040.0	228.1
1194.0	193.2	20380.0	233.8
1672.0	198.6		

Table XXIII—Nitromethane.

v.	μ_v.	v.	μ_v.
8.99	9.01	646.4	47.95
13.31	10.02	938.2	56.12
18.64	11.15	1306.0	64.66
27.06	12.76	1907.0	75.24
37.89	14.52	2670.0	85.92
55.00	16.89	3876.0	99.68
77.00	19.38	5426.0	114.5
111.8	22.55	7876.0	131.5
156.5	26.15	11030.0	147.3
227.1	30.55	16010.0	162.5
318.1	35.37	22410.0	181.3
461.6	41.45		

Table XXIV—Orthonitrophenol.

v.	μ_v.	v.	μ_v.
366.2	82.76	6963.0	190.6
542.3	95.11	8604.0	192.8
759.3	106.6	10380.0	203.9
938.2	114.0	15060.0	213.3
1131.0	120.7	21090.0	222.5
1642.0	135.3	26060.0	226.2
2299.0	148.3	31420.0	230.3
2841.0	157.1	45610.0	234.9
3426.0	164.5	63860.0	240.1
4973.0	178.7		

Table XXV—Benzaldehyde.

v.	μ_v.	v.	μ_v.
15.53	1.695	133.0	3.385
23.00	1.950	193.1	3.736
32.20	2.198	270.3	4.058
46.74	2.493	392.4	4.328
65.45	2.770	549.4	4.561
95.00	3.078		

Discussion of Results.

Besides the measurements above given, quantitative determinations of the molecular conductivity of potassium iodide, sodium iodide, ammonium iodide, cuprous iodide, silver bromide, silver nitrate, lead iodide, mercuric iodide, mercuric chloride, zinc iodide, cupric nitrate, iodine, sulphur, parani-

trophenol, dinitrophenol, trinitrophenol, vanilline, ethyl formate, ethyl acetate, metallic potassium, and metallic lithium have also been made, but the results are not given here for the reason that the measurements were made in an earlier form of apparatus which did not permit of sufficient accuracy of measurement. Qualitative tests have been made on several hundred substances, which show that all soluble salts and a great variety of organic compounds form conducting solutions.

Binary Salts.—The limit of molecular conductivity of binary salts in solution in ammonia at —38° lies between 270 and 340 Kohlrausch units. This is more than twice the maximum conductivity of the same salts in water solutions at the ordinary temperature, and is far above the conductivity of electrolytes in any other known solvent. At 100°, however, the limit of molecular conductivity in aqueous solution is somewhat greater[1] than the maximum conductivity of the same salts in solution in ammonia at its boiling-point.

The values for the maximum molecular conductivities of a number of salts in five of the best electrolytic solvents are given in the following table, which is made up from data taken from Dutoit and Friderich,[2] and from Carrara,[3] together with values obtained for ammonia solutions by the authors.

	Acetone.	Aceto-nitrile.	Methyl alcohol.	Water.	Ammonia.
NaI	140	160	90	121	...
NaBr	...	...	88	122	302
KI	154	...	98	143	340?
KBr	...	...	97	144	340
NH_4I	153	...	105	143	...
NH_4Cl	...	...	100	144	304
KNO_3	...	...	...	133	338
NH_4NO_3	...	...	...	114	297
$AgNO_3$	...	160	...	121	280?
HCl	2.21	...	133	360	...

Notwithstanding the fact that for the most part ammonia solutions conduct electricity with greater facility than do

[1] Krannhals: Ztschr. phys. Chem., **5**, 250 (1890); and Schaller: *Ibid.*, **25**, 497 (1898).

[2] Bull. Soc. Chim. (3), **19**, 336 (1898).

[3] J. Chem. Soc. Abstracts, **72**, II, 471 (1897).

water solutions of the same concentration, the solute in ammonia is dissociated to a much less extent than it is in water. The accompanying table shows, for nine salts dissolved in these two solvents, the dilution at which the dissociation reaches respectively 50, 75, and 90 per cent.

Solute	Degree of dissociation.	Water.	Ammonia.
KI	0.50	....	80
	0.75	0.4	400
	0.90	20.0	2000
KBr	0.50	....	100
	0.75	....	800
	0.90	20.0	4000
KNO_3	0.50	0.5	200
	0.75	5.0	1200
	0.90	25.0	5000
NaBr	0.50	....	125
	0.75	....	500
	0.90	32.0	2500
$NaNO_3$	0.50	0.5	....
	0.75	5.0	800
	0.90	33.0	4000
NH_4Cl	0.50	....	250
	0.75	1.0	1500
	0.90	25.0	5000
NH_4Br	0.50	....	75
	0.75	....	700
	0.90	....	3500
NH_4NO_3	0.50	....	100
	0.75	....	500
	0.90	....	4000
$AgNO_3$	0.50	0.6	125
	0.75	5.0	350
	0.90	40.0	1500

Aqueous solutions of binary salts practically reach their limit of molecular conductivity at a dilution of 1,000 to 5,000 liters, while ammonia solutions must be carried to a dilution of 25,000 to 50,000 to come as near the limit. In accordance with the Thomson-Nernst hypothesis, this behavior of ammonia solutions was to be expected from the low dielectric constant as found by Goodwin and Thompson[1], and later by Cool-

[1] Phys. Rev., 8, 38 (1899).

idge.[1] The low degree of dissociation is also in accordance with measurements of the boiling-point elevations of ammonia solutions of salts.[2] At the concentrations at which these measurements were made the dissociation is so low that it would be difficult to detect the effect of dissociation on the rise of the boiling-point of a solvent with such a low constant of molecular elevation as that of ammonia.

The very high conductivity of ammonia solutions seems hence to be due to the high velocity of migration of the ions as a result of the low viscosity of the solvent.

Ostwald's law of dilution holds approximately for ammonia solutions of a number of binary salts, the only solutes which have so far been tested. The constant diminishes in value with the dilution but the change is of a very different order from that which is found in the case of water solutions of the same salts. The values for the constants for three salts, calculated from the formula

$$K = \frac{\alpha^2}{(1-\alpha)v},$$

in which the symbols have their usual significance, are given below for both ammonia and water. The values for the water solutions are calculated from Koh lrausch's data.[3]

Ammonium Chloride.

a.	NH_3.	H_2O.
52.30	0.1919	....
58.00	0.1809	....
62.89	0.1760	49.68
65.89	0.1662	45.47
68.64	0.1628	38.54
73.81	0.1553	22.86
78.58	0.1536	11.53
81.09	0.1533	5.981
83.25	0.1481	5.527
87.08	0.1445	3.777
90.20	0.1460	2.506
92.26	0.1568	1.749
93.91	0.1932	1.264
96.05	0.1897	0.8435

[1] Wied. Ann., **69**, 130 (1899).
[2] The Authors: This JOURNAL, **20**, 852 (1898).
[3] Leitfähigkeit der Electrolyte, p. 159.

Potassium Nitrate.

a.	NH_3.	H_2O.
57.00	0.2277	12.79
62.12	0.2074	11.55
66.85	0.2006	10.20
70.02	0.1970	9.528
72.48	0.1906	8.754
77.41	0.1826	6.269
81.32	0.1740	4.509
83.66	0.1706	4.006
85.59	0.1677	3.389
89.15	0.1623	2.893
91.66	0.1635	2.332
93.15	0.1664	1.885
94.30	0.1699	1.710
95.28	0.1444	1.443

Potassium Bromide.

a.	NH_3.	a.	NH_3.
61.76	0.330	90.47	0.210
66.94	0.303	93.12	0.220
71.06	0.279	94.97	0.210
73.81	0.269	96.67	0.222
76.09	0.260	97.79	0.250
80.02	0.237	98.56	0.315
84.10	0.235	98.81	0.321
86.12	0.228		

Silver Halides.—Measurements of the conductivity of the halides of silver is a matter of interest in view of the fact that, because of their resistance to the action of most ordinary solvents,[1] their conductivities have not been measured.

Silver iodide in solution in ammonia is a good conductor, but it is not as strongly dissociated as is the nitrate of silver, a fact which is not unexpected when the behavior of mercuric chloride and the halides of some other heavy metals in resisting the dissociating action of water is recalled.

Mercuric Chloride.—This salt reacts with liquid ammonia to form mercuriammonium chloride, but since at the same time a small quantity of an insoluble compound was formed, quantitative measurements of the conductivity of mercuriammonium solutions have not yet been made.

[1] According to St. v. Laszczynski and St. v. Gorski [Ztschr. Electrochem., 4, 290 (1897)], a pyridine solution of silver iodide is a non-conductor of electricity.

The results of a brief investigation of the action of liquid ammonia on mercuric chloride may be given here. When mercuric chloride is sealed up in a tube with liquid ammonia, a heavy liquid of the composition represented by the formula

$$HgCl_2.2NH_3.10NH_3$$

is formed, as is shown by the following analytical data :

I. 2.0000 grams mercuric chloride united with 1.4033 grams ammonia. The compound thus formed lost 1.1679 grams ammonia at 20°.

II. 3.0000 grams mercuric chloride united with 2.0638 grams ammonia. The compound thus formed lost 1.6882 grams ammonia at 20°.

	Calculated for $HgCl_2.2NH_3.10NH_3$.	Found. I.	II.
NH_3 lost at 20°	35.79	34.32	33.56
" retained at 20°	7.15	6.92	7.41

The liquid, which is slightly soluble in ammonia, has a specific gravity of 1.56, and is stable only under pressure. At low temperatures it solidifies, and the solid formed melts at —9°. If the pressure is removed from this solid, 10 molecules of ammonia are dissociated off, and there remains behind a compound of the formula $HgCl_2.2NH_3$, which seems to be identical with mercuri-diammonium chloride. The compound melts with some decomposition, as does the fusible white precipitate. Mercuri-diammonium chloride, prepared by precipitation from a solution of mercuric chloride in a concentrated solution of ammonium chloride, when sealed in a tube with liquid ammonia, takes up 10 molecules of ammonia to form the heavy liquid described above.

Mercuric Cyanide.—This salt is very easily soluble in ammonia, even deliquescing in the vapor from the cold liquid. In water, mercuric cyanide is not at all dissociated,[1] while in ammonia it forms a solution possessed of a distinct conductivity. The molecular conductivity, however, instead of increasing, decreases with the dilution. The decrease is small, and the rate diminishes as the dilution becomes greater. Three independent measurements on different specimens of the salt gave similar results in this respect.

[1] Ostwald : Wissenschaft Grundlag. d. analyt. Chem., p. 147 (1894).

No instance in which the molecular conductivity decreases with dilution is known in aqueous solution, but such behavior has been observed in the case of certain ether and amyl alcohol solutions[1] and in the case of solutions in benzonitrile.[2]

Silver Cyanide.—Silver cyanide is readily soluble in ammonia, forming a solution which is a fair conductor. As is true of mercury cyanide, the molecular conductivity of the salt is low and varies but slightly[3] with changes in the concentration. Contrary to the behavior of mercury cyanide, however, the molecular conductivity of silver cyanide increases somewhat with the dilution.

Ternary Salts.—But one ternary salt, strontium nitrate, has been measured. It has a much higher molecular conductivity than the binary salts, and although the dilution was carried beyond $v = 100{,}000$, the limit was not reached, the ammonia solution behaving in this respect like aqueous solutions of the ternary salts.

Phenols.—Phenol, the cresols, the dihydroxybenzenes, pyrogallol, and guaiacol form solutions which show a distinct conductivity, while solutions of ortho- and paranitrophenol, dinitrophenol, and picric acid approach salt solutions in their power to conduct the current. Accurate quantitative measurements have been made on orthonitrophenol only, which, as the data given in the tables show, is a very much better conductor in ammonia than in water.[4]

Nitrohydrocarbons.—The aromatic nitrohydrocarbons are, so far as they have been tested,[5] more or less soluble in ammonia, forming solutions which in some cases are brilliantly colored. Solutions of nitrobenzene and of the nitrotoluenes are but slightly colored and conduct the current but little, if at all, while dinitrobenzene and trinitrotoluene approach the salts in their conducting power.

Dinitrobenzene.—The interesting observation was made upon this substance that the conductivity of its solution upon dilu-

1 Kablukoff: Ztschr. phys. Chem., **4**, 429 (1889).

2 Euler: *Ibid.*, **28**, 623 (1899).

3 Euler (*loc. cit.*) has observed that the molecular conductivity in nitrobenzene solutions increases but slightly, if at all, with increasing dilution.

4 Bader: Ztschr. phys. Chem., **6**, 296 (1890).

5 This JOURNAL, **20**, 832 (1898).

tion did not at once come to its full value, but that the resistance dropped continuously for about half an hour, the total fall amounting to about 2 or 3 per cent. After reaching its full value the resistance remained constant. In one experiment the resistance, after becoming constant, did not change perceptibly after the lapse of fourteen hours. The only analogous case recorded is an observation by Euler,[1] who noticed that when solutions in nitrobenzene were diluted the conductivity did not become constant until after some time, the total increase in this case amounting to about 10 per cent. It was also observed that the blue color of the freshly prepared ammonia solution gradually changes to a fine red.

It is worth while to note that contrary to the behavior of dinitrobenzene, no appreciable time was necessary for the solution of trinitrotoluene to take on its final conductivity value upon dilution.

Nitromethane.—Nitromethane, which is miscible with ammonia, is not dissociated to as great an extent as are the aromatic nitro compounds, but it nevertheless forms a good conducting solution. While nitromethane itself is but very slightly soluble in water, it very readily dissolves in a solution of an alkaline hydroxide, forming a compound in which the metal takes the place of hydrogen in the nitromethane.[2] No record of measurements of the conductivity of the salts of nitromethane or of nitromethane itself in aqueous solution could be found.

Basic and Acid Amides.—The amides of potassium, sodium, and lithium are fair conductors of electricity in ammonia solution as are also a considerable number of acid amides.

Of the class of basic amides, measurements of the molecular conductivity have been made only in the case of sodamide. In preparing the solution of sodamide a weighed quantity of metallic sodium was introduced into the resistance cell, when by the action of the ammonia, the metal was soon changed into sodamide. The end of the reaction was recognized by the complete disappearance of the blue color of the sodammonium, and by the final constant value of the resistance of the

[1] Ztschr. phys. Chem., **28**, 619 (1899).

[2] Meyer und Jacobson: Lehrb. d. organ. Chem., **1**, 254 (1893).

solution. The difficulty of weighing metallic sodium accurately makes a confirmation of the values given in the table above desirable, a matter which will have the attention of one of us in the near future. Quantitative measurements of the conductivity of potassamide and lithamide solutions have also been made. Sodamide is slightly soluble in ammonia; potassamide is very soluble.

The acid amides generally dissolve readily in ammonia, most of them forming solutions which are conductors. They vary a great deal, however, in the extent of dissociation which they undergo; benzamide and paracettoluide, for example, do not conduct the current perceptibly, acetamide and urea conduct very poorly, while succinimide conducts well, and metanitrobenzenesulphonamide approaches the salts in the facility with which its solution conducts the current.

The only measurements so far recorded of the conductivity of acid amides in aqueous solution are those of Bader[1] on a number of substituted cyanamides, of Walden[2] on succinimide, and of Trübsbach[3] on a few ureides. The substituted cyanamides and some of the substituted ureides form solutions which are fairly good conductors, while the solutions of succinimide, urea, and some simple ureides are very poor conductors. Qualitative measurements by the authors on a number of acid amides, including acetamide and benzenesulphonamide, justifies the conclusion that in general this class of bodies is but slightly dissociated in aqueous solution. On the other hand, ammonia has the power of dissociating many of them to a very considerable extent, as the measurements given above show. An interesting question in connection with these solutions is whether the positive ion is hydrogen or ammonium. From the action of ammonia on hydrogen ions in aqueous solution it is to be presumed that the positive ion is ammonium, but if this is the case it would seem that the dissociation curves of these substances might be expected to follow more closely the curves for salts, instead of resembling, as they do, those of weak acids in aqueous solution. If ammonium salts are formed in solution they are so unstable that,

[1] Ztschr. phys. Chem., **6**, 304 (1890).
[2] *Ibid.*, **8**, 484 (1891).
[3] *Ibid.*, **16**, 708 (1895).

on evaporating away the solvent and warming up to the laboratory temperature, they decompose, leaving behind the free acid amides.[1] On the other hand, if the positive ion is hydrogen, then the migration of the positive ion is strikingly low.[2]

Reactions of the Amides in Liquid Ammonia.—If acid and basic amides bear to ammonia a relation analogous to that borne to water by the ordinary oxygen acids, then, since the former are dissociated in liquid ammonia, they should react in ammonia something after the manner of acids and bases in water.

Numerous reactions suggest themselves, a few of which take place in aqueous solution while others have been carried out in benzene and other non-electrolytic solvents.[3] Titherly especially, in his investigations on the action of sodamide on a variety of substances, has prepared a number of salts of acid amides. By continued heating of benzene solutions of formamide, acetamide, propionamide, and benzamide, respectively, with sodamide, Titherly obtained sodium formamide, HCONHNa, sodium acetamide, $CH_3CONHNa$, sodium propionamide, $C_2H_5CONHNa$, and sodium benzamide, $C_6H_5CONHNa$.

Only a few such reactions have yet been studied in ammonia solution, and these only qualitatively.

If an ammonia solution of benzenesulphonamide is allowed to act on sodamide, after a time a well-crystallized substance separates from the solution which is presumably benzenesulphonamide in which sodium is substituted for amide hydrogen.

Solutions of benzenesulphonamide, succinimide, benzoic sulphinide, acetamide, and urea dissolve metallic sodium, metallic magnesium, and, to some extent, metallic zinc, with the evolution of hydrogen, and well-crystallized products separate from the solutions. The amount of hydrogen given off

[1] This statement was proved by experiment to be true in the cases of benzoic sulphinide, acetamide, and benzenesulphonamide. Orthonitrophenol retains 1 molecule of ammonia. Trinitrotoluene retains 3 molecules of ammonia.

[2] Hydrochloric acid in acetone shows an abnormally low conductivity. Carrara: Ztschr. phys. Chem., **27**, 184 (1898).

[3] Dessaignes: Ann. Chem. (Liebig), **82**, 231 (1852); Strecker: *Ibid.*, **103**, 324 (1857); Gal: Bull. Soc. Chim., **39**, 647 (1883); Curtius: Ber. d. chem. Ges., **23**, 3037 (1891); Blacher; *Ibid.*, **28**, 432 and 2352 (1895); Titherly: Jour. Chem. Soc. (London), **71**, 461 (1897).

when magnesium was dissolved in a solution of acetamide, was measured and found to be equivalent to the amount of magnesium dissolved. In the case of the action of magnesium on benzenesulphonamide the volume of hydrogen obtained was much less than the calculated amount, a fact which may have its explanation in the reducing action of the nascent hydrogen on the acid amide.

Silver oxide dissolved sparingly in a solution of acetamide, and copper oxide dissolved in a solution of benzoic sulphinide; after a time well-crystallized substances separated from the solutions, and these were presumably silver and copper salts of acetamide and benzoic sulphinide, respectively.

In this connection the fact may also be mentioned that, in general, the salts of ammonium, which bear to ammonia a relation in some respects analogous to the relation which the oxygen acids bear to water, dissolve the alkali metals and magnesium, and in some cases other metals, with the evolution of hydrogen. Ammonium nitrate, for example, dissolves magnesium very energetically and after a time a well-crystallized product separates from the solution.

Further, on the basis of the relations which the ammonium salts and the acid amides on the one hand, and the metallic amides on the other, bear to ammonia as an electrolytic solvent, it ought to be possible to find indicators which give color reactions in ammonia after the manner of indicators in aqueous solutions. Such indicators in fact exist.

Phenolphthalein dissolves in ammonia forming a pale-red solution. Addition of sodamide greatly intensifies the color of the solution, while in turn the color is completely discharged by addition of benzoic sulphinide or ammonium bromide.

Carmine dissolves sparingly, forming a dirty red solution which sodamide changes to a fine blue. The blue color is changed to a fine red by the addition of ammonium bromide.

Saffranine dissolves abundantly, forming a beautiful crimson solution. Sodamide or potassamide changes this color to blue, and acid amides or ammonium salts restore the crimson color.

The strong colors of a considerable number of other sub-

stances in solution in ammonia, among which may be mentioned metadinitrobenzene, trinitrotoluene, and orthonitrophenol are but slightly affected by either the addition of basic or acid amides. A large excess of an ammonium salt of an acid amide changes the blue solution of alizarin to a mixed color.

The Alkali Metals.—The most remarkable observations made in connection with the work on liquid ammonia is the fact that solutions of the alkali metals conduct electricity with great facility, without any separation of products at the electrodes and without the least sign of polarization. The authors have confirmed the statements of Cady[1] to this effect. The greatest difficulty in the way of measuring the conductivity of these solutions lies in the fact that the metals react with the solvent rapidly enough to introduce a large and uncontrollable error. For example 56 mg. of sodium in 45 cc. of ammonia at its boiling-point, were completely changed into sodamide in the course of fifteen minutes. An approximate value of the molecular conductivity of a sodium solution was obtained by introducing a known weight of sodium into the resistance cell of the conductivity apparatus, and as soon thereafter as possible, taking a reading of the resistance. This gave for $v = 18.56$, a molecular conductivity of 392.6, or if the molecule be assumed to contain 2 atoms of sodium, as some previous investigators[2] on these solutions indicate, then the molecular conductivity becomes 785.2.

An attempt was made to determine what change, if any, takes place in the molecular conductivity on diluting the solution. To this end the above solution was again measured and, as rapidly as possible, ammonia was added from the receiver until the second point in the conductivity cell was covered. The solution was then stirred and the resistance read. The molecular conductivity calculated from these two measurements was for $v = 1856$, $\mu_v = 332.6$; and for $v = 27.49$, $\mu v = 335.4$. Approximate measurements made by Cady[3] gave for $v = 4.28$, 3.97, and 3.8, $\mu_v = 420$, 441, and 479,

[1] J. phys. Chem., **1**, 707 (1897).
[2] Joannis: Compt. rend., **115**, 820 (1898).
[3] *Loc. cit.*

respectively. Certainly the molecular conductivity does not change much with the dilution. Because of a mishap to the apparatus, further measurements on these solutions have not yet been made.

An attempt was also made to measure the temperature coefficient of the alkali metal solutions, but here too the action between the metal and the solvent[1] interposed a serious difficulty which was only partially overcome by making the measurements at temperatures much below the boiling-point of ammonia at atmospheric pressure. Under these conditions the temperature which could not be at all accurately determined was found to be between 0.5 and 1.5 per cent per degree, and to be of positive sign.

As stated above, Joannis has shown that in these metallic solutions 2 atoms of the metal are united with 2 molecules of ammonia to form, for example in the case of sodium, a compound having the formula $Na_2N_2H_6$, to which he has given the name sodammonium. It has not been shown, however, that the ammonia combined with the metal in this compound plays the same part as does ammonia in the ammonium compounds. The solution behaves in many respects as a simple solution of the metal in ammonia in which the former is combined with the ammonia rather after the manner of substances with water of crystallization than as a constituent of a stable compound of the ordinary kind. Or the ammonia is coordinated with the metal in the sense in which Werner uses this expression. Water of crystallization in combination with compounds has no effect on the conductivity of their aqueous solutions, nor does it take part in the reactions of the compounds as ordinarily considered. The same is in all probability true of salts with ammonia of crystallization in ammonia solutions. It may be doubted therefore whether the compound sodammonium has any further analogy with the hypothetical compound ammonium than the fact that it may be brought under the same formula.

The following facts seem to indicate that sodium solutions

[1] By comparing the rate of reaction between sodium and ammonia on the one hand, and sodium and water on the other, some idea of the relative number of hydrogen ions present in liquid ammonia is obtained. The number must be very much less in ammonia, which is in agreement with the high resistance found for the pure liquid.

occupy a very interesting position between ordinary electrolytic conductors and some vapors.

J. J. Thomson[1] has shown that sodium vapor is blue, that it conducts electricity remarkably well, and without polarization at the electrodes, properties which an ammonia solution of sodium likewise exhibits. While, however, in the form of vapor the molecule and atom of the alkali metals are identical,[2] in solution in ammonia the molecule contains 2 atoms.[3]

Whatever may be the nature of the substance in solution, it conducts the current with remarkable facility. It would seem that the process of conduction must consist in the wandering of charged bodies through the solution, and the fact that the temperature coefficient is of positive sign and of considerable magnitude lends probability to this view.

As there are molecules of but one kind in solution it is impossible to assume that 1 molecule should be able to take on only a positive charge and another only a negative charge. Consequently it would seem that one and the same particle must be able to take on a charge of either positive or negative electricity with which it wanders to the oppositely charged electrode, there to loose its charge and to take on one of opposite sign, or meeting an oppositely charged particle to thus lose its charge.[4] At any rate enormous quantities of electricity may pass through such solutions without producing any visible effects other than a deepening of the blue color in the vicinity of the electrodes in dilute solutions.

Investigations on these metal solutions will be continued during the present year by one of us (Kraus) in the laboratories at Johns Hopkins University.

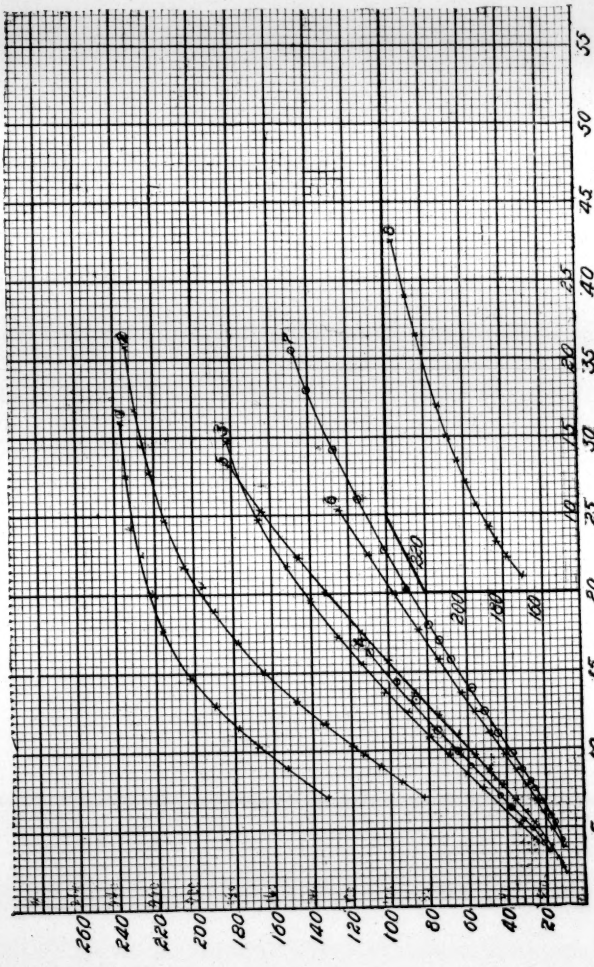
In the appended plates, in which the ordinates represent molecular conductivities and the abcissae the cube roots of the dilution, the dependence of the molecular conductivity upon the dilution of the solutions is shown graphically.

[1] Phil. Mag. (5), **29**, 441 (1890). It is interesting to note in this connection that sodium chloride which has been heated in the vapor of sodium takes on a permanent blue color. (Geisel: Ber. d. chem. Ges., **30**, 158 (1897).)

[2] Scott: Trans. Roy. Soc., Edinburgh, **14**, 410 (1887).

[3] Joannis: *Loc. cit.*

[4] This is approximately the hypothesis upon which J. J. Thomson explains the conductivity of the vapor of sodium and some other substances. (*Loc. cit.*)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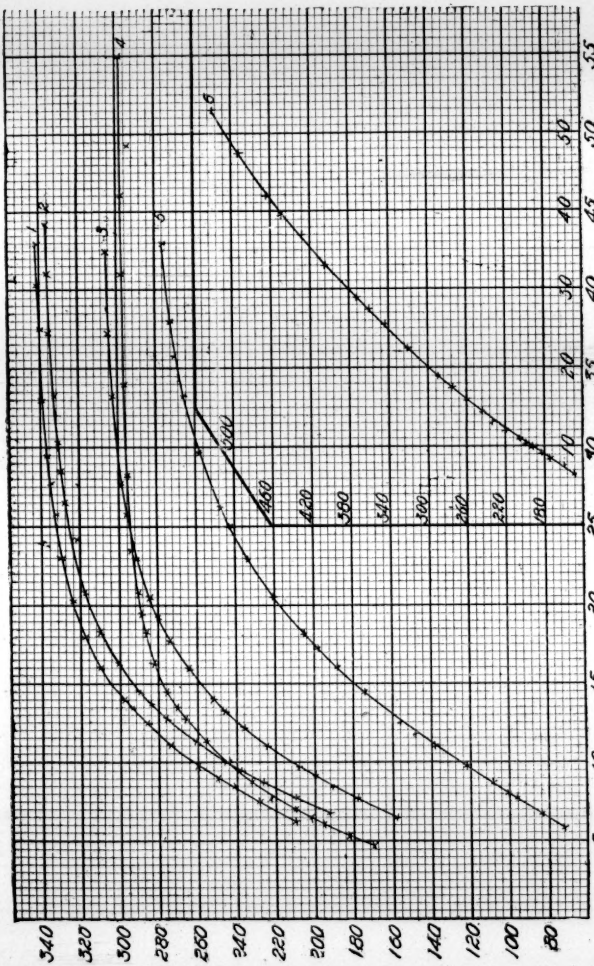
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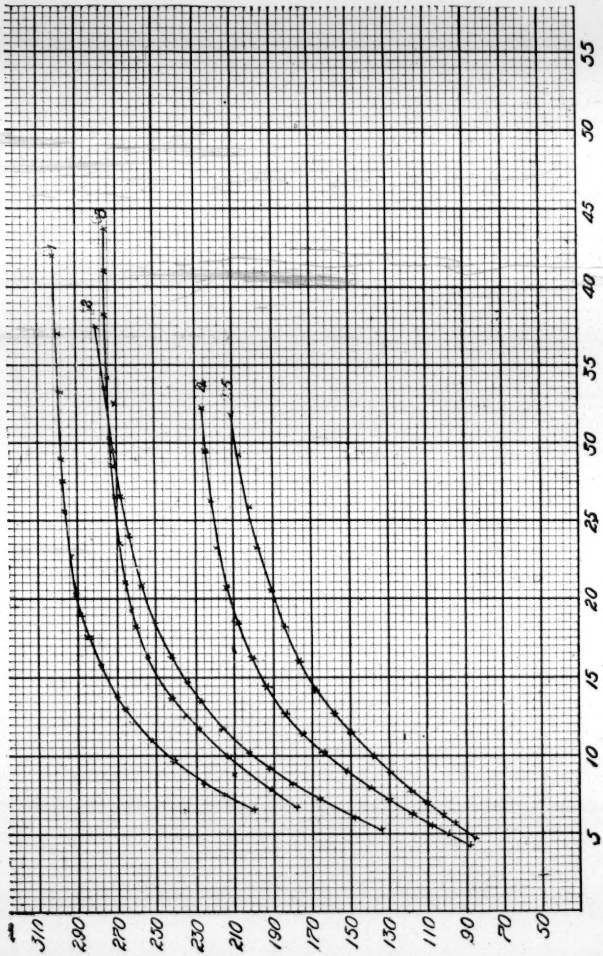
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Summary of Results.

The results of the work described in this paper may be briefly summed up as follows :

1. The problem of obtaining pure liquid ammonia has been successfully solved and a form of apparatus has been constructed which is well adapted to the study of the conductivity of liquids of low boiling-points.

2. With a few exceptions salts are dissociated to a less degree in ammonia than in water.

3. The limit of molecular conductivity of binary salts in ammonia at —38° ranges from about 290 to 340 Kohlrausch units, which is much above the conductivity of the same salts in solution in water at 18°.

4. Ostwald's law of dilution holds approximately for binary salts. Other solutes have not been tested.

5. Silver iodide is dissociated in ammonia solution, although not to so great an extent as other binary salts.

6. Mercuric chloride reacts with ammonia to form the compound $HgCl_2.12NH_3$, which loses 10 molecules of ammonia on being warmed up at atmospheric pressure. The compound $HgCl_2.2NH_3$ is identical with mercuri-diammonium chloride.

7. Mercuric cyanide and silver cyanide conduct in ammonia, but the conductivity in neither case changes much with the dilution. The molecular conductivity of the former falls slightly, the latter rises somewhat.

8. The one ternary salt measured has a high molecular conductivity, and, as in water solution, it approaches its maximum more slowly than do the binary salts.

9. Many of the nitro compounds are good conductors in ammonia solution. Some of them approach the binary salts in their power to carry the current.

10. The acid and basic amides generally dissolve in ammonia to form good conducting solutions. The conducting power of the acid amides ranges from the fraction of a unit to that of the binary salts.

11. The acid and basic amides may be considered as acid and bases derived from ammonia in the same manner as the

oxygen acids and bases are derived from water. This relation is borne out by the chemical behavior of the amides in solution in ammonia and by their action on color indicators.

12. As found by Cady ammonia solutions of the alkali metals conduct electricity without polarization at the electrodes. The conductivity changes but slightly, if at all, with the concentration.

These solutions exhibit positive temperature coefficients.

In conclusion, the authors wish to express their appreciation of the kindness of Professor Lucien I. Blake in placing at their disposal the facilities of the Department of Physics and Electrical Engineering.

THE UNIVERSITY OF KANSAS,
LAWRENCE, September, 1899.

ON THE CAUSE OF THE EVOLUTION OF OXYGEN WHEN OXIDIZABLE GASES ARE ABSORBED BY PERMANGANIC ACID.

BY H. N. MORSE AND H. G. BYERS.

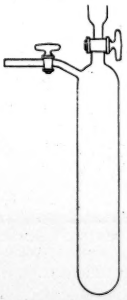
It was suggested in a former communication[1] that the evolution of oxygen which occurs when hydrogen or carbon monoxide is absorbed by acidified solutions of potassium permanganate is due to the action of the peroxide which is formed upon the excess of the permanganic acid; and, further, that the cause of this action of the oxide upon the acid may be a tendency on the part of the simpler peroxide molecules to polymerize to more complex ones at the expense of the acid.

It was affirmed by V. Meyer and M. von Recklinghausen[2] that when hydrogen and carbon monoxide are absorbed by a neutral solution of potassium permanganate, there is no liberation of oxygen. Previous to this, however, it had been stated by one of us[3] that "the reduction of potassium permanganate by the superoxide in a neutral solution is too slow for convenient observation." If, now, the evolution of oxygen which occurs when gases are absorbed by acidified solu-

[1] Morse and Reese: This JOURNAL, **20**, 721.
[2] Ber. d. chem. Ges., **29**, 2551.
[3] This JOURNAL, **18**, 413.

tions of permanganate is due to the action of the oxide on the permanganic acid, as maintained by us[1] in opposition to V. Meyer and H. Hirtz,[2] then the oxide which is formed in neutral solutions and is *inactive* should become *active* whenever —after the disappearance of the gas—the solution containing the oxide in suspension is acidified. Our experiments show, as regards carbon monoxide, that when this gas is absorbed by neutral solutions of permanganate, there is no evolution of oxygen; but when an acid is afterwards added, there is an evolution of oxygen similar in all respects to that which is observed when an equal volume of the gas is absorbed by an acidified solution of permanganate of the same concentration.

Again, if the cause of the reduction of the acid is, as suggested, the tendency on the part of the peroxide to become more complex at the expense of the acid, then the evolution of oxygen should gradually diminish in rapidity as the polymerization progresses. Our experiments prove that as a matter of fact the rate of evolution does constantly decrease whether the gas is absorbed in an acid solution or in a neutral one which is afterwards acidified. It is shown, moreover, that when the gas is absorbed in an acid solution the period of rapid evolution does not terminate with the disappearance of the gas as it should if the gas is the direct cause of the liberation of oxygen.



Finally, if polymerization of the oxide is the cause of the decomposition of the acid, the quantity of the gas absorbed remaining fixed, the volume of oxygen liberated within a given time should increase with increasing concentration of the permanganic acid. Our experiments show that it does so increase.

The apparatus which was employed by us is shown in the accompanying figure. It consisted of a glass tube having a capacity of 100 cc. The liquid reagents were introduced through the larger horizontal stop-cock at the top, and the gas through the stop-cock in the nearly capillary side-tube.

[1] This JOURNAL. **20**, 521.

[2] Ber. d. chem. Ges., **29**, 2828.

To make room for the gas within, a volume of air equal to, or somewhat greater than, that of the gas to be introduced was first withdrawn from the tube. To secure proper mixing of the contents and a uniform condition of temperature, the tubes were attached transversely to a shaft which passed through a thermostat and was revolved at the rate which appeared to secure the greatest agitation of the contents of the tube. A nearly constant temperature of 35° was maintained in the bath. The gas experimented with was carbon monoxide, of which 12 cc.—or the volume which would reduce to that under standard conditions of temperature and pressure—were employed in every case. With this fixed volume of carbon monoxide, various quantities of potassium permanganate were agitated both in neutral and in acidified solutions. The volume of the acidified solutions, however, was always raised to 50 cc. by the addition of water. 12 cc. of carbon monoxide reduce 56.44 mgms. of potassium permanganate to the peroxide condition, and the weights of the salt introduced into the tubes were always some multiple of this quantity. Hence the oxide resulting from the absorption of the gas and the excess of permanganic acid bore to each other in every case definite, known, molecular ratios. For example, when 169.32 (= 56.44 × 3) mgms. of the salt were agitated with 12 cc. of the gas, the ratio of $HMnO_4$ to MnO_2 was 2 to 1; and when 1549.64 (= 56.44 × 31) mgms. of the salt were used, the ratio was 30 to 1. The ratios actually employed were 2 : 1, 5 : 1, 10 : 1, 15 : 1, 20 : 1, 25 : 1, 30 : 1, and in one case 7.5 : 1. In working with acidified solutions, the same degree of acidity was always produced, the quantity of sulphuric acid which was added being in every instance equivalent to the potassium in the permanganate reduced by the gas plus three times the potassium in the excess of the salt. The amount of the reduction was measured by titrating the contents of the tubes, after agitation, against standard solutions of oxalic acid or of potassium tetroxalate.

Our first step was to determine the length of time required to absorb the gas by neutral solutions of various concentrations. The results are given in Table I.

Table I.

Ratio of $HMnO_4$ to MnO_2.	Time of agitation. Hours.	CO unabsorbed. cc.	Apparent reduction. cc. of O_2.
2 : 1	5	1.0	—0.08
	5	0.85	—0.10
	9	0.2	0.01
	9	0.4	—0.01
	10	0.0	—0.02
	10	0.0	—0.01
5 : 1	3	0.6	—0.14
	3	0.2	—0.00
	4	0.2	—0.02
	4	0.4	0.03
	5	0.0	0.03
	5	0.0	0.03
10 : 1	1½	1.3	—0.13
	1½	1.5	—0.13
	2	0.0	—0.13
	2	0.0	—0.26
20 : 1	1	0.4	—0.26
	1	0.9	—0.87
	1½	0.4	—0.07
	1½	0.0	0.00
	2	0.0	0.00
	2	0.0	—0.53
30 : 1	1	0.3	—0.09
	1	0.2	0.26
	1¼	0.0	0.17

Having found the time which neutral solutions of various concentrations required for the complete absorption of the gas, we proceeded to ascertain what would happen if, after the absorption, the solutions were acidified. In Table II, which gives the conditions and results of our experiments in this direction, the duplicates are bracketed together, and letters are employed to indicate what tubes were in the bath at the same time.

Table II.

Ratio of $HMnO_4$ to MnO_2.		Hours of agitation. Neutral.	Acid.	Oxygen liberated. cc.	Percentage reduction.
2 : 1		11	24	0.89	7.34
		11	24	0.98	8.37
		22	24	1.16	9.76
		22	24	0.98	8.37
		26	24	1.06	8.92
		26	24	1.14	9.65
		13½	150	5.67	47.51
		13½	150	5.66	47.39
5 : 1	a	4	24	1.88	6.29
	a	4	24	1.45	4.87
	a	24	00	0.06	....
	a	24	00	0.11	....
	b	24	24	1.68	5.67
	b	24	24	1.74	5.84
	b	48	00	0.06	....
	b	48	00	0.06	....
		4	150	7.44	24.85
		4	150	7.44	24.85
10 : 1	c	2	24	2.09	3.51
	c	2	24	2.15	3.57
	c	24	00	—0.13	....
	c	24	00	—0.06	....
	d	24	24	2.29	3.82
	d	24	24	2.35	3.89
	d	48	00	0.00	....
	d	48	00	0.06	....
		3	150	11.46	18.33
		3	150	11.17	18.04
20 : 1	e	1½	24	3.40	2.84
	e	1½	24	3.54	2.94
	e	25½	00	0.13	....
	e	25½	00	0.07	....
	f	24	00	0.00	....
	f	24	00	—0.33	....
	f	2	24	3.00	2.50
	f	2	24	3.00	2.50
	g	24	24	3.24	2.61
	g	24	24	3.75	3.01
	g	48	00	—0.06	....
	g	48	00	0.06	....
		2	24	3.34	2.77
		2	24	4.00	3.33
		2	150	11.62	9.69
		2	150	12.95	10.78

30 : 1	h	1¼	24	4.56	2.54
		1¼	24	5.10	2.86
	h	24	oo	—0.09	....
		24	oo	—0.17	....
	i	24	24	4.74	2.62
		24	24	5.42	3.01
	i	48	oo	0.35	....
		48	oo	0.52	....
		2	150	18.40	10.10
		2	150	19.27	10.84

We next proceeded to determine how long a time acidified solutions of permanganate of different concentrations require for the absorption of the gas, and what volumes of oxygen are liberated previous to the disappearance of the last traces of the gas. Table III gives the results:

Table III.

Ratio of $HMnO_4$ to MnO_2.	Time of agitation. Hours.	CO unabsorbed. cc.	O_2 liberated. cc.	Percentage reduction.
2 : 1	5	0.85	0.22	1.76
	6	0.60	0.28	2.25
	7	0.35	0.29	2.51
	8	0.0	0.34	2.85
	8	0.0	0.34	2.85
5 : 1	2	1.65	0.73	2.39
	2	0.95	0.53	1.41
	3	0.0	0.88	2.92
	3	0.0	0.88	2.92
10 : 1	1½	0.55	1.65	2.71
	1½	0.20	1.40	2.27
	2	0.0	1.84	3.04
	2	0.0	1.65	2.73
20 : 1	1	2.6	2.80	2.31
	1	0.9	2.80	2.33
	1½	0.0	3.33	2.77
	1½	0.0	3.74	3.11
30 : 1	1	0.30	5.27	2.92
	1¼	0.0	5.36	2.98
	1¼	0.0	5.63	3.00

Finally, we absorbed the gas in acid solutions of various concentrations, agitated for periods of 6, 24, and 150 hours, and determined the amount of oxygen which had been liberated. The results are contained in Table IV.

Table IV.

Ratio of $HMnO_4$ to MnO_2.	Time of agitation. 6 hours. O_2 liberated. cc.	6 hours. Per cent reduction.	24 hours. O_2 liberated. cc.	24 hours. Per cent reduction.	150 hours. O_2 liberated. cc.	150 hours. Per cent reduction.
2 : 1	CO not all absorbed		0.80	6.85	1.91	16.02
			0.73	6.10	2.49	20.81
			0.72	6.07		
			0.71	5.95		
5 : 1	a 1.49	4.96	b 2.46	8.21	c 3.88	12.99
	1.35	4.46	2.30	7.64	3.88	12.99
$7\frac{1}{2}$: 1	c 1.90	4.25	e 2.77	6.16	c 5.80	12.91
	1.90	4.25	2.77	6.16	5.96	13.25
	a 2.06	4.37	d 2.77	6.16		
	...	...	2.94	6.49		
10 : 1	d 2.93	4.90	e 3.57	5.95	c 7.80	13.05
	2.63	4.90	3.57	5.95	...	....
	f 3.20	5.34	g 3.84	6.43	h 7.80	13.05
	2.89	4.84	3.84	6.43	7.64	12.79
	3.20	5.34	3.87	6.49		
	3.13	5.21	4.14	6.87		
15 : 1	f 3.84	4.21	5.26	5.78	h 9.54	10.47
	3.87	4.24	5.26	5.78	9.70	10.84
20 : 1	f 4.79	3.99	5.89	4.89	l 10.75	8.86
	5.13	4.29	5.75	4.75	11.44	9.51
	i 5.10	4.24	k 5.30	4.38	h 10.81	8.99
	4.62	3.68	...	...	....	...
	4.95	4.14	k 5.74	4.72	10.81	8.99
	5.30	4.38	5.89	4.90	11.03	9.16
25 : 1	i 5.90	3.92	k 6.06	4.02	l 13.66	9.09
	5.90	3.92	6.37	4.24	14.30	9.39
30 : 1	i 6.38	3.53	k 7.48	4.15	l 15.25	8.46
	6.53	3.56	7.48	4.15	16.83	9.36
			7.32	4.06		

It appears from Table I that when carbon monoxide is absorbed by a neutral solution of potassium permanganate there is no liberation of oxygen during the absorption; and from certain experiments included in Table II, where no acid was added, it appears that the neutral permanganate may be agi-

tated for many hours with the peroxide which is produced in it by the absorption of the gas without suffering any sensible reduction. The inactive state of the oxide under these conditions may be due to the fact that the salt is more stable than the acid, or to the fact that the peroxide precipitated in a neutral solution contains large quantities of potassium and is therefore already saturated ; or, what is more likely, the failure to liberate oxygen may be due to both of these causes. As regards the quantity of alkali which such an oxide may contain, it has been shown[1] that when a neutral solution of the permanganate undergoes complete, so-called spontaneous reduction to the peroxide, the precipitate contains the whole of the potassium.

Table II shows that when carbon monoxide has been absorbed by an excess of neutral permanganate, giving an inactive oxide, and the liquid is afterwards acidified, there is a liberation of oxygen just as when the gas is absorbed by an acid solution. Moreover, the general characteristics of the reaction are the same in both cases, pointing to a common cause. The amount of oxygen liberated within a given time increases with the concentration of the acid, and the rate of evolution in any given case decreases with time, the decrease being most marked in the more concentrated solutions. These phenomena are most easily explained by supposing the peroxide molecule in its simpler state to be unsaturated in the sense that it is capable of uniting with other molecules of its own kind and that its power to do this enables it to break up adjacent molecules of permanganic acid. Its failure to liberate oxygen when formed in neutral solutions would be explained, as previously stated, by the fact that when it is so formed it is in combination with potassium.

Table III shows that when a fixed quantity of carbon monoxide is absorbed by acid solutions of permanganate, the quantity of oxygen which is liberated during the absorption increases with the concentration of the solution. This result was anticipated and the experiments were made with a view to testing the hypothesis as to the cause of the liberation of oxygen. It was reasoned that if the reduction of the acid is

[1] This JOURNAL, 18, 411.

due to the inclination of the peroxide molecules to abstract still other molecules of the oxide from the acid in order to unite with them, then the rate of the reduction, and consequently of the liberation of oxygen, should increase with the concentration of the permanganic acid.

From Table IV it appears that the quantity of oxygen which is liberated in a given period *after* the gas has disappeared increases with the concentration just as it does during the absorption, and as it does also when the gas is first absorbed in a neutral solution to which acid is afterwards added. Moreover, the rate of evolution diminishes with time in the former as it does in the latter case. Nevertheless, the evolution is still relatively rapid for a time—especially in the more dilute solutions—after the disappearance of the gas, as if the causes of the evolution during the absorption and afterwards were identical. These relations will be rendered clearer by an inspection of Table V, in which the averages of the results contained in Tables III and IV are given :

Table V.

Ratio of $HMnO_4$ to MnO_2.	Time required for the absorption of the CO.	O_2 evolved during the absorption of the gas.	Percentage reduction during the absorption of the gas.	Agitation. 6 hours. O_2 evolved.	Agitation. 6 hours. Percentage reduction.	Agitation 24 hours. O_2 evolved.	Agitation 24 hours. Percentage reduction.	Agitation. 150 hours. O_2 evolved.	Agitation. 150 hours. Percentage reduction.
	Hours.	cc.		cc.		cc.		cc.	
2 : 1	8	0.34	2.85	...	...	0.74	6.24	2.20	18.42
5 : 1	3	0.88	2.92	1.42	4.71	2.38	7.93	3.88	12.99
$7\frac{1}{2}$: 1	..	...	...	1.95	4.29	2.81	6.24	5.88	13.08
10 : 1	2	1.75	2.89	3.05	5.09	3.81	6.35	7.75	12.99
15 : 1	..	...	...	3.86	4.23	5.26	5.78	9.62	10.66
20 : 1	$1\frac{1}{8}$	3.54	2.94	4.82	4.12	5.71	4.73	10.97	9.11
25 : 1	..	...	...	5.90	3.92	6.22	4.13	13.98	9.24
30 : 1	$1\frac{1}{4}$	5.50	2.99	6.45	3.55	7.43	4.12	16.04	8.91

A comparison of Tables II and IV will show that the oxide formed in acidified solutions is, in general,—especially in the more concentrated ones—more active during the first twenty-four hours than that formed in neutral solutions ; while if the agitation is continued for one hundred and fifty hours, the latter

oxide exhibits, in all cases, the greater activity. Table VI, in which averages are given, will show this more clearly.

Table VI.

Ratio of $HMnO_4$ to MnO_2.	24-hour period. Acid. O_2 cc.	24-hour period. Neutral. O_2 cc.	150-hour period. Acid. O_2 cc.	150-hour period. Neutral. O_2 cc.
2 : 1	0.74	1.03	2.20	5.67
5 : 1	2.38	1.69	3.88	7.44
10 : 1	3.81	2.22	7.55	11.29
20 : 1	5.71	3.38	10.97	12.28
30 : 1	7.43	4.95	16.04	18.84

If we grant that the evolution of oxygen, when the peroxide is agitated with an acidified solution of permanganate, is due to the abstraction of more peroxide from the acid with subsequent polymerization, and that the decline in the activity of the oxide is a consequence of such polymerization, the question naturally arises whether polymerization may not also take place between those molecules which are formed in consequence of the oxidation of the gas, as well as between these and others which must be derived from neighboring molecules of the acid. The experience of V. Meyer and M. von Recklinghausen[1] seems to indicate that such a polymerization may occur. It was found by them that when hydrogen or carbon monoxide is allowed to stand quietly over an acidified solution of permanganate, there is little liberation of oxygen; in other words, the agitation of the gas with the solution is essential to any considerable evolution of oxygen. The explanation which we would suggest for this phenomenon is that the absorption and oxidation of the gas taking place only at the surface of the liquid, the solution becomes dilute at that point, and the molecules of peroxide therefore unite with each other to a great extent instead of with molecules of oxide derived from the acid. It may be due in part to the same cause that the evolution of oxygen during the absorption of the gas is so much more rapid in concentrated than in dilute solutions.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
February, 1900.

[1] *Loc. cit.*

Contribution from the Chemical Laboratory of Wesleyan University.

ABSORPTION APPARATUS FOR ELEMENTARY ORGANIC ANALYSIS.

By Francis Gano Benedict.

Since the time of Liebig, granulated calcium chloride and potassium hydroxide solution have been almost universally used for the absorption of water and carbon dioxide, respectively, in elementary organic analysis. Numerous forms of apparatus for holding these reagents have been devised but no satisfactory substitute for either absorbent has been generally accepted. In a former article[1] a special form of soda-lime that had given satisfactory results in the absorption of carbon dioxide was described, and it was mentioned that sulphuric acid was used to absorb the water formed in the process of the combustion. In the system here described sulphuric acid is used as the absorbent of water and soda-lime as the absorbent of carbon dioxide.

A fundamental error of most absorbing systems, including the one described in the article referred to, is the unequal drying which the gases receive on entering and leaving the carbon dioxide absorber. All dehydrating agents have not the same absorptive power, and hence a gas dried by one reagent will differ considerably in absolute moisture content from that dried by another. It is essential in determining the correct weight of carbon dioxide that no moisture be added to or removed from the absorbing system. In the earlier forms no provision was made to collect the moisture carried away by the gas which passes through a potash bulb, as it was considered that the moisture and carbon dioxide of the air used in the final aspiration, counterbalanced any error arising from evaporization of moisture.[2] As generally conducted at present the gas dried by fused calcium chloride enters the potash bulb and escapes through a small extension tube containing fragments of solid potassium hydroxide, and, while it is true that the issuing gas is thereby dried, it is by no means true

[1] J. Am. Chem. Soc., **21**, 389.

[2] Die Entwicklung der organischen Elementaranalyse, W. Dennstedt. p. 21.

that it is dried to the same degree as it was before entering the carbon dioxide absorbing system. Where the greatest refinement of method is not required this unequal drying may be considered negligible. In the method of combustion in oxygen gas, already referred to,[1] but a small quantity of gas (700 to 1000 cc.) issues from the carbon dioxide absorbers, and consequently the error is not great. Where, however, a current of air instead of oxygen is used in the combustion, sufficient gas may pass through the system to exert a material influence on the result if the gas is unequally dried.

While doubtless different drying agents produce the greatest differences in the absolute amount of moisture remaining in a gas, the same drying agent will not always produce the same result, and as Dudley and Pease[2] have said, the mechanical condition as well as the freshness of calcium chloride may be a serious source of error when two different forms of this reagent are used for drying the gas before and after leaving the absorber.

Calcium chloride, being a solid, has many advantages over sulphuric acid, a liquid, for the absorption of water vapor. It is, however, not without its disadvantages. Probably the greatest difficulty in its use is the fact that it often contains basic chlorides, which absorb carbon dioxide as well as water. This impurity is so constantly present that it becomes necessary to pass dry carbon dioxide through a freshly filled calcium chloride tube for several hours before the basicity is destroyed. It is then necessary to remove the carbon dioxide by passing a current of dry air through the tube for some time. But as Winkler[3] has shown, this operation of saturating the calcium chloride is not thoroughly remedial since it is only the surface of the lumps of calcium chloride that is thus saturated, and later, as the solid absorbs water and deliquesces, fresh surfaces of basic chlorides are exposed and consequently carbon dioxide retained.

Moreover, calcium chloride deliquesces when used for some time, and the semiliquid portions are liable to clog the tube

[1] J. Am. Chem. Soc., **21**, 389.
[2] *Ibid.*, **15**, 540.
[3] Ztschr. anal. Chem., **31**, 545.

and prevent the passage of the gas. A number of years ago Löwe[1] suggested a simple remedy for this, however, which consists in greasing the inside of the U-tube with clean tallow, and thus preventing the liquid from adhering to the walls.

Concentrated sulphuric acid, though a liquid reagent, has advantages that would seem to outweigh those of calcium chloride for use as an absorbent. It is a much better dehydrating agent than calcium chloride, does not retain carbon dioxide, and, in addition, serves to indicate the rate of passage of the gas. In an actual experiment to show the great avidity of this reagent for water, 64 grams of ordinary commercial concentrated sulphuric acid contained in a Drechsel gas washing bottle removed nearly 11 grams of water from an air current passing at the rate of 1 liter per minute. Less than 0.1 gram remained unabsorbed in the air leaving the absorbing bottle.

A property of sulphuric acid which is often of value in making combustions, is the fact that if unburned carbonaceous volatile products escape from the combustion tube they are mainly retained by the sulphuric acid, which soon becomes blackened. This indication often saves much time in forestalling unnecessary weighing and calculating.

In combustions of most organic substances more water is generally formed than is sufficient to saturate the gas leaving the combustion tube; hence, a varying amount of water condenses about the stopper in the exit end of the tube. The water formed in the process of a combustion is generally collected in a U-tube having a bulb on the arm nearest the combustion tube, which serves to collect the condensed water and thus to prevent unnecessary exhaustion of the absorbing agent. As this bulb fills it may be emptied, and consequently a number of combustions may be made with the same absorbing tube. The Volhard and the Marchand form of U-tube are most commonly used.

In the absorber indicated in the figure a small glass vial placed in one limb of a plain 5-inch U-tube $\frac{5}{8}$ of an inch in diameter serves the purpose of the bulb in the earlier forms. This vial, which should be 3 or 4 mm. less in diameter than the

[1] Ztschr. anal. Chem., **11**, 403.

U-tube, is so supported on a bit of glass rod flattened at one end that the glass tube conducts the products of combustion into the neck of the vial. Water condensing in the tube falls in drops to the bottom of the vial and the gas saturated with aqueous vapor at the temperature of the apparatus passes through the U-tube into the carbon dioxide absorbers.

A plug of coarse glass-wool is inserted in the other arm and extends from the cork to the point where the bend begins. Enough commercial concentrated sulphuric acid is slowly

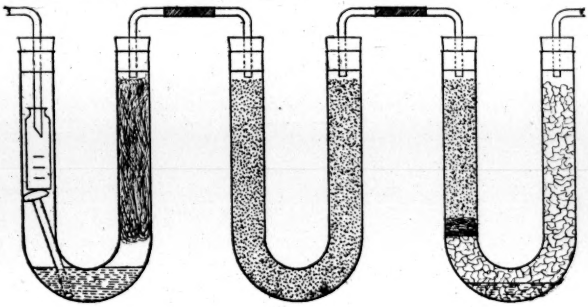


Fig. 1.

poured through the glass-wool to saturate it thoroughly and just seal the bend at the bottom of the U in such a way that the gas will have to bubble through it. The lower end of the glass-wool will then be about 1 centimeter above the surface of the liquid, the air space preventing too much acid from being carried up mechanically into the glass-wool. When this happens it is not unusual for the acid to be carried over into the carbon dioxide absorbers. The air space is otherwise valuable as it permits isolation of each bubble and consequently better regulation of the rate of the combustion. If the bend is just sealed, the minimum pressure only is necessary to force the gas through the tube. The greater part of the water vapor is retained by the acid in the bend of the tube as the gas bubbles through, while the last traces are removed by the acid adhering to the glass-wool. Thus in one plain U-tube are incorporated three distinct drying operations;

condensation of excessive moisture, removal of the major part of the water vapor, and final absorption of remaining traces of moisture. The tubes are closed with well-fitting, one-holed rubber stoppers furnished with glass elbows. One elbow extends far enough below the stopper to be thrust into the neck of the vial. The tubes are finally closed with short bits of red rubber tubing fitted with short glass plugs. Inasmuch as all the tubes in the absorbing train can be used for a number of combustions before refilling, the rubber stoppers can be replaced by corks which are crowded down and cut off flush with the ends of the U-tube. The corks may then be coated with sealing-wax. This precaution was not taken in the determinations reported in the following article. Rubber stoppers gave entire satisfaction. A tube prepared in this manner may safely be relied on to absorb about 1 gram of water vapor exclusive of the water condensed in the vial. In a series of experiments on the combustion of sugar where approximately 0.12 gram of water was weighed each time, it was found that about three-fourths of the water condensed in the vial. No direct estimate can be made, however, on the length of time such a tube will last, though if the vial is marked with a file scratch at the points indicating cubic centimeters and the amount of condensed water deducted from the increase in weight of the tube, a ready check on the amount of water vapor actually absorbed is at hand.

This form of absorber is characterized by great efficiency. As sulphuric acid is a much stronger dehydrating agent than calcium chloride, less moisture remains in the air current. Repeated tests have shown that all the moisture that can be retained by sulphuric acid will be absorbed in such a tube when the air current is much faster than would ever be permissible in the process of a combustion (150 cc. per minute), a rapidity of desiccation unattainable with calcium chloride. The use of a liquid absorbent renders the attachment of a special apparatus to indicate the rate of flow unnecessary. Where potassium hydroxide solution is used to absorb the carbon dioxide no indicator is needed, but in systems using solid absorbents for both water and carbon dioxide it has been customary to insert between the combustion tube and the

water-absorbing tube a small U-tube containing either mercury, water, or sulphuric acid[1] to note the rate of flow.

This form of U-tube is very easy to wipe dry with a cloth while other forms, including as they do bulbs and enlargements, are not so readily cleaned.

The friability of many other forms of drying apparatus is not shared by this form. Plain glass U-tubes are not, of course, indestructible, but when properly handled the risk of breakage is very small, while if broken they can be replaced at one-half the cost of any other form.

The carbon dioxide absorbing system is a slightly modified form of that described in the article previously referred to,[2] and consists of a U-tube containing specially prepared soda-lime followed by a U-tube one-third filled with soda-lime and two-thirds filled with pumice stone saturated with concentrated sulphuric acid. This differs from the earlier form in the substitution of the pumice stone and sulphuric acid for calcium chloride as a final dryer in the train. The actual amount of moisture leaving a soda-lime tube is small, not more than 3 to 5 mgms. per liter of gas escaping from the absorbers, and of this quantity the greater portion would be retained by calcium chloride, as was found by repeated tests, but of necessity there would still be a loss of moisture amounting to from 0.5 to 1 mgm., that in accurate work should not be neglected. Sulphuric acid, on the other hand, retains all of the moisture, *i. e.* the issuing gas is dried to the same extent as that which enters.

The soda-lime is practically a mixture of equal weights of sodium hydroxide and calcium oxide to which sufficient water has been added to slake the lime and dampen the whole mixture. The preparation of this form of soda-lime is very simple. One kilogram of commercial caustic soda "Greenbank Lye" is dissolved in 750 cc. of water in an iron kettle and 1 kilogram of finely-pulverized quicklime is added to the solution with constant stirring until the lime is slaked and the water is all absorbed. The product is then broken into lumps

[1] Monatshefte(1889), 398; Ann. Chem. (Liebig), **285**, 385; Ztschr. anal. Chem., **11**, 403.

[2] J. Am. Chem. Soc., **21**, 389.

and, after cooling, placed in securely sealed bottles. For use it should be damp but not so moist that the particles glisten in strong light. If too dry it is easily moistened by adding a few drops of water and rubbing up in a mortar. If too much water is accidentally added the mixture may be brought to the proper consistency by the addition of dry soda-lime. The finished product should be pulverized as finely as is consistent with the passage of the gas. For use in the carbon dioxide absorbers the pieces should not be larger than 2 mm. in diameter. As the soda-lime is damp there is no danger that particles will be carried along mechanically with the gas.

The second tube of the carbon dioxide absorbing system serves the dual purpose of retaining any moisture lost from the first soda-lime tube and any traces of carbon dioxide that might escape absorption in the first tube in case it became exhausted. With soda-lime the change in color is a very accurate indication of the absorption of carbon dioxide, and hence it is only necessary to replace the tube with a fresh one before it has been completely whitened.[1] The increase in weight of the second tube is ordinarily not more than 7 mgms. for each combustion, and, consequently, when the increase is greater it is an additional sign that the first tube is nearly exhausted.[2] It has been the custom in this laboratory to use the first tube until the increase in weight of the second tube is more than 10 mgms. One arm and the bend of the second tube of the carbon dioxide absorber is filled with dry lump pumice stone. Concentrated sulphuric acid is then allowed to trickle slowly down over the pumice until it becomes thoroughly saturated, but there must not be acid enough left in the bottom of the U-tube to seal the bend. A 10 mm. layer of glass-wool is then laid over the pumice-stone in the partially filled arm and the remaining space filled with soda-lime. The glass-wool must not come in contact with acid at any point.

In case sufficient carbon dioxide to exhaust the soda-lime does not enter the tube, it should last for 25 or more combustions, since the sulphuric acid would completely absorb at

[1] J. Am. Chem. Soc., **21**, 394.

[2] A tube freshly filled with soda-lime will last for from 6 to 14 combustions, the number depending on the size of the lumps of soda-lime, the quantity in the tube, and the weight of carbon dioxide absorbed in each combustion.

least 0.5 gram of water; and if 10 mgms. were retained from each combustion the possible efficiency would be 50 combustions. The ease with which the last tube is prepared, however, renders it more satisfactory to change it after 25 or 30 combustions.

An absorbing system consisting of three separate pieces necessitates, it is true, an additional weighing with its delays and possible error. While the introduction of error in weighing the third tube cannot be avoided, this form of water absorber does away with the necessity of shaking the water out of the bulb after each weighing, and consequently a weighing with its possible source of error is avoided. The number of weighings required is the same in each case. Furthermore, in many forms the carbon dioxide absorber is in two pieces, and, in such cases, the advantage in accuracy and weighing lies with the system under consideration.

Aside from the great efficiency of the absorbing agents which have been discussed elsewhere[1] the greatest advantage to be derived from this form of absorber is the ability to make accurate analyses independent of the weather. The condensation of moisture, not to speak of gases on the surface of potash bulbs and other similar forms of absorbers, is a fluctuating factor dependent on atmospheric conditions, and it has been considered impossible by some[2] to make accurate determinations of carbon and hydrogen in damp or stormy weather. That the condensation of moisture on the surface of the absorbing system is not a negligible factor is seen from the precautions ordinarily given to wipe the absorber and allow it to stand in the balance room for at least half an hour. While doubtless this procedure gives a close approximation to correct results, the differences in the amount of condensation, on days in which the atmospheric conditions are not the same, are very considerable. When the conditions to which the glass is exposed in the course of a combustion are considered, *i. e.*, the wiping, the handling with moist fingers, the sojourn of at least an hour in close proximity to a combustion furnace, together with the considerable internal heat from the absorp-

[1] *Loc. cit.*, p. 393.

[2] J. Am. Chem. Soc., **15**, 451; and **20**, 528.

tion of the carbon dioxide by the reagent, the assumption that the surface condition remains the same after as before, even with all precautions, is rather broad.

It is possible, however, to have constant surface conditions before and after analysis. By carefully wiping the absorber with clean, dry cheese-cloth it is possible to clean the apparatus till there is no longer any loss in weight. This point is taken as the standard condition, and the tubes are so wiped before and after each combustion. In an operation of this kind, the simpler the form of the absorber and the smaller the surface, the more readily can the apparatus be brought into condition for weighing. Such a method would be impossible when applied to a Liebig or Geissler potash bulb.

The operation as practiced in this laboratory with many hundred combustions, including those reported in the accompanying paper, is as follows: A piece of stout copper wire is so bent as to hang on the arm of the balance and act as a hook on which a U-tube can be readily supported. The rubber plugs are removed from the first U-tube, which is then wiped thoroughly with a piece of clean, dry cheese-cloth in each hand in such a way that the glass does not come in contact with the fingers. It should receive a very hard, thorough rubbing. The tube is then placed on the balance and brought to equilibrium and then removed, thoroughly wiped again, and weighed. It will probably lose somewhat in weight. The operation is continued until the weight remains constant. After a little experience it is seldom necessary to wipe the tube more than three times. No difficulty was experienced with the electric charges noted by Miller.[1] The tube is then plugged and the weight recorded. At the end of the combustion the operation is repeated and the condensation on the surface of the glass thereby eliminated. The importance of using clean, dry cheese-cloth cannot be too much emphasized. A tube so cleaned rapidly increases in weight owing to the condensation on its surface, but the increase is not too rapid to prevent making an accurate record of the weight.

To make an especially efficient purifier for the air or oxygen used in the combustion, the reagents may conveniently

[1] J. Am. Chem. Soc., **20**, 428.

be placed in a calcium chloride jar. The gas is conducted through sulphuric acid placed in the lower compartment of the jar, through soda-lime filled in around a large glass tube thrust through the constriction, and after descending to the bottom of the jar, issues over a long column of pumice-stone drenched with concentrated sulphuric acid. The details of construction are shown in Fig. 2.

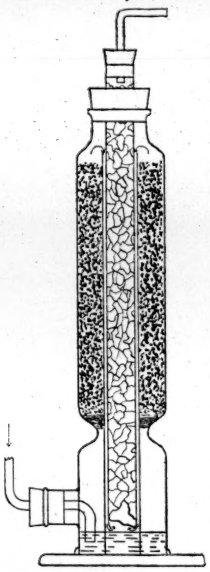


Fig. 2.

A "12-inch" calcium chloride jar, preferably with the tubulature as near the top of the lower compartment as possible, is selected, and a piece of glass tubing, of an external diameter a little less than the internal diameter of the constriction in the jar, is cut off long enough to rest on the bottom, and to reach to within 30 mm. of the top of the jar. A cork on the end of a glass rod is loosely inserted in the upper end of the tube and a layer of glass-wool or long-fiber asbestos is packed around the tube to a depth of 3 or 4 mm. Soda-lime prepared as described above and pulverized into pieces approximately 2 mm. in diameter is then introduced, and the jar filled to within 1 centimeter of the top of the inner tube. A "12-inch" jar will require about 175 grams of soda-lime. A long glass tube, approximately 10 mm. external diameter, is thrust through the one-holed rubber stopper inserted in the mouth of the jar. This tube is slightly tapered at the lower end and is filled with pumice-stone, which is subsequently drenched with concentrated sulphuric acid. The glass tube extends from about 10 mm. above the stopper to within 20 mm. of the bottom, and should be of a diameter small enough to slide easily through the upright tube passing through the constriction in the jar. The upper end of the tube is closed with a one-holed red rubber stopper carrying a

glass elbow and a piece of rubber tubing with a screw pinch-cock. This stopper may be sealed with paraffin or wax if desired.

Concentrated sulphuric acid is poured down the central tube, thoroughly drenching the pumice-stone and collecting in the base. The first lot of acid should be poured out of the tubulature and finally sufficient acid poured through the tube to fill the lower compartment to within 5 mm. of the one-holed rubber stopper which has been inserted in the tubulature. The cork is then replaced in the upright tube and the screw pinch-cock closed. A glass tube bent downward is thrust through the hole in the rubber stopper in the tubulature in such a manner that a current of gas passing through it bubbles through the acid in the base of the jar. The gas then rises, passing through a long column of soda-lime at a very slow rate, turns and passes down through the annular space between the two glass tubes, and finally, entering the base of the tube filled with pumice-stone, issues at the top. The greater portion of the water is removed as the gas bubbles through the acid; the carbon dioxide is completely removed by the soda-lime and the unabsorbed moisture, including that lost from the slightly moist soda-lime, is removed as the gas passes over the pumice-stone and sulphuric acid. The gas issuing at the top is free from carbon dioxide and as free from moisture as is possible with sulphuric acid.

The ordinary form of "12-inch" calcium chloride jar has the tubulature in such a position that about 20 cc. of acid can be introduced without flowing out of the orifice or coming in contact with a rubber stopper inserted in the tubulature. A jar having the tubulature nearer the top is preferable and may be obtained at a slight increase in cost.[1] The chief advantage of the form of jar having the tubulature near the top of the base is that there is less liability of getting concentrated acid on the rubber stopper in the tubulature. The extra amount of acid that can be placed in the lower compartment increases the length of service of the purifier, but 20 cc. of acid will, it is calculated, remove 6 grams of water vapor from the air. If

[1] Whitall, Tatum & Co., of Philadelphia, have furnished the writer with several 12-inch jars with the tubulature inserted at various specified points, with but slight addition to the price of stock jars.

the temperature of the gasometer is taken as 28° C., the gas leaving it would contain 27 mgms. of water vapor per liter. An average of 1.5 liters of oxygen are used for each combustion in the method as here conducted, hence the amount of acid conveniently placed in the base of a regular "12-inch" jar would suffice for 200 combustions.

In case the sulphuric acid should become exhausted, it is only necessary to drain the acid out of the lower compartment through the tubulature and pour fresh acid through the tube containing pumice-stone to regenerate the purifier. This is done in this laboratory after every 50 combustions. The soda-lime need not be renewed until it becomes three-fourths white.

MIDDLETOWN, CONN.

Contribution from the Chemical Laboratory of Wesleyan University.

THE ELEMENTARY ANALYSIS OF ORGANIC SUBSTANCES CONTAINING NITROGEN.

BY FRANCIS GANO BENEDICT.

The chemical processes involved in organic elementary analysis where the combustion of a substance is made with cupric oxide are, as a rule, extremely simple. When carbon and hydrogen, with or without oxygen, are the only elements in the substance, the carbon is burned to carbon dioxide and the hydrogen to water. When, however, the molecule contains nitrogen the reaction is not so regular, for while in many cases all of the nitrogen is liberated uncombined, in certain classes of compounds a portion, at times a no inconsiderable portion, is combined with the oxygen of the molecule, of the gaseous medium, or of the cupric oxide, in the form of nitric oxide, which in the presence of free oxygen forms nitrogen peroxide. This latter compound, whose presence is shown by the appearance of red fumes in the exit end of the combustion tube and by the acidity of the water condensed in the small bulb of the water-absorbing tube, introduces a serious error in the determination of carbon and hydrogen, owing to its solubility in most of the reagents ordinarily used for the absorption of water and carbon dioxide. While in many in-

stances the influence of this abnormality is so slight as to be unimportant, its possibilities are great enough to necessitate special modifications of the methods of combustion to eliminate the errors caused by the formation and the subsequent absorption of the oxides of nitrogen. Especially is this true in determining the composition and the nature of organic substances of fundamental importance, compounds which serve as the basis of new theories in organic chemistry. It is in such instances that the vital importance of the greatest degree of accuracy in organic analytical operations is apparent.

Owing, perhaps, to its technical importance, the determination of carbon has been brought to a state of perfection rarely attained by the methods of analytical chemistry. The technical methods for the determination of carbon are, however, not readily applicable in the analysis of organic compounds and, furthermore, in most technical methods of analysis no provision is made for the determination of hydrogen; but the determination of hydrogen is of almost as great, if not of equal, importance and the method most commonly used in the laboratory for the determination of carbon, *i. e.*, combustion with cupric oxide in a current of air or oxygen, permits of the determination of hydrogen.

The formation of oxides of nitrogen in the combustion of organic substances containing nitrogen by the cupric oxide method was first noted by Gay-Lussac.[1] Nitrogen, while ordinarily a most inert substance, unites at high temperatures with the oxygen of the air to form nitric oxide. This phenomenon is readily observed in all cases of combustion in air where a high temperature is attained.

In the method of combustion adopted in the work here reported the substance is first charred in the closed tube, *i. e.*, with no current of air or oxygen, and, after complete charring, oxygen is admitted to oxidize the non-volatile residue, and the copper that has been reduced by the volatile products of the dry distillation. As the oxygen is admitted the carbon ignites and glows, and here it is true there may be a temperature sufficiently high to cause a union of the nitrogen in the tube with the oxygen. That no appreciable quantities of

1 Ann. Chim., **95**, 184; **96**, 53.

oxides of nitrogen[1] are formed in this way, is seen by the fact that they cannot be detected when non-nitrogenous organic substances yielding carbonaceous residues are burned in a current of air or oxygen.

In considering the formation of the oxides of nitrogen in the combustion tube it is necessary to subdivide all organic nitrogenous substances into two classes: one in which the nitrogen is attached to an oxygen atom, and the other in which no oxygen is connected with the nitrogen. To the first class belong nitro, nitroso, isonitroso, and azoxy bodies, oximes, etc., while the second class includes practically all other nitrogenous organic compounds: amines, amides, nitriles, etc.

The bodies belonging to the first class would be expected to yield oxides of nitrogen all the more readily as the nitrogen is to a certain extent partially oxidized, and nitro compounds, according to this assumption, owing to the high state of oxidation of the nitrogen atom, would serve as types of the substances which would most readily liberate their nitrogen in the oxidized form.

In the amido and other unoxidized nitrogen compounds on the other hand, it would be necessary to have an actual oxidation of the nitrogen atom to obtain oxides of nitrogen. In an examination of the influence of the method of combustion on the formation of the oxides of nitrogen it was found that in burning urea, for example, in a current of oxygen, *i. e.*, without previous charring in the closed tube, the oxides of nitrogen were formed to such an extent as to cause the presence of red fumes in the absorbing system. Obviously in this case there was a direct oxidation of the nitrogen and at a comparatively low temperature. Other amidic compounds gave similar results.

In the absolute determination of nitrogen by mixing the substance with finely pulverized cupric oxide and burning in a vacuum, Klingemann[2] found in the case of certain oxygen-free azines and glyoxalines that very considerable quantities of the oxides of nitrogen were formed. In this case the

[1] The general term 'oxides of nitrogen' is applied to all products formed by the reaction between nitric oxide, oxygen, and water.

[2] Ber. d. chem. Ges., **22**, 3066.

nitrogen must have come from the compound and the oxygen from the copper. Klingemann explains the formation of the oxides of nitrogen as the action of the nascent nitrogen on the copper oxide. It is interesting to note the evidence presented by Klingemann to support the theory that the use of a copper spiral in the regular carbon and hydrogen determination of substances containing nitrogen is unnecessary.

O. F. Tower[1] has shown in an admirable treatment of the subject that amidic nitrogen bodies, of which urea, hippuric acid, and *p*-toluidine are taken as types, when burned in the manner described on p. 335, yield no appreciable quantities of oxides of nitrogen. Nitro bodies, such as dinitrobenzene and nitraniline, also yield, according to his results, no oxides of nitrogen. Trinitrophenol, on the other hand, liberates sufficient quantities to affect materially the percentage of both carbon and hydrogen.

In burning the amidic and "unoxidized nitrogen" compounds in a closed tube, the combustion apparently proceeds as follows: The substance, if not volatilized unchanged, undergoes dry distillation, and the gases given off reduce the first portions of the cupric oxide in the combustion tube. If any oxides of nitrogen are formed, they are decomposed in the presence of the reducing gases, the carbonaceous residue, and the reduced copper. After dry distillation is complete, the greater portion of the nitrogen is probably in the gaseous form, though the charred residue may, according to some writers, contain considerable quantities of nitrogen.

In volatile substances the combustion is practically all accomplished by the oxygen of the cupric oxide, though it is possible that portions of the volatilized material, when passing through the hot reduced copper, may be decomposed by the heat with a deposition of carbon.

Nitro and allied bodies, on the other hand, yield, when burned as above, nitric oxide in appreciable quantities. According to the investigations of Liebig,[2] Klingemann,[3] and Tower,[4] nitric oxide is probably the only oxide of nitrogen

[1] J. Am. Chem. Soc., **21**, 596.
[2] Pogg. Ann., **18**, 357.
[3] Ber. d. chem. Ges., **22**, 3066.
[4] J. Am. Chem. Soc., **21**, 596.

formed directly in the combustion of nitrogenous substances. By means of secondary reactions with oxygen and water, there may be formed almost any or all of the oxides of nitrogen, the chief of which is, however, nitrogen peroxide.

Nitric oxide itself would have no material influence on the operation, for it is not absorbed by any of the reagents commonly used in this analytical process; *i. e.*, concentrated sulphuric acid or fused calcium chloride for the absorption of water vapor, or concentrated potassium hydroxide solution or soda-lime for the absorption of carbon dioxide.

Nitrogen peroxide, however, is always formed by the union of nitric oxide with the oxygen in the tube or in the absorbing system, and is absorbed by all the above reagents except calcium chloride, thereby introducing the error.

In many cases the amount of oxides of nitrogen is not large, and consequently is all retained by the sulphuric acid when this reagent is used to absorb water, though in highly nitrated bodies, especially those burning with explosive violence, the percentage of carbon is often increased by the absorption of the oxides of nitrogen in the carbon dioxide absorber.

A large number of combustions of oxidized and unoxidized nitrogenous bodies were made to determine, if possible, the cause of the variations in the amounts of the oxides of nitrogen. The analyses were made by first charring the material in the closed tube; *i. e.*, without the current of oxygen which was finally admitted at the end of the combustion, each combustion requiring about one hour for completion. The modified form of purifying apparatus and absorbing system described in the preceding paper were used in all analyses.

Jena glass combustion tubes have given excellent satisfaction, four tubes having withstood the heating in 97, 99, 104, and 116 combustions, respectively.

Table I gives a series of analyses of a number of pure substances burned with this method without the use of the copper spiral, those of non-nitrogenous substances being added for a dual purpose; *i. e.*, first to show the accuracy of the method of analysis and second to show the purity of the products used in some subsequent operations.

Table I.

Substance.	Weight taken. Gram.	Weight water found. Gram.	Weight carbon dioxide found. Gram.	Hydrogen. Found. Per cent.	Hydrogen. Theory. Per cent.	Carbon. Found. Per cent.	Carbon. Theory. Per cent.
Sucrose	0.2028	0.1175	0.3129	6.48	6.48	42.08	42.08
$C_{12}H_{22}O_{11}$.	0.2011	0.1161	0.3103	6.46	....	42.08	....
	0.2262	0.1317	0.3488	6.51	....	42.06	....
Benzoic acid,	0.1414	0.0629	0.3566	4.98	4.95	68.78	68.88
C_6H_5COOH.	0.1419	0.0638	0.3581	5.03	....	68.83	....
	0.1443	0.0646	0.3639	5.01	....	68.78	....
Naphthalene,	0.1049	0.0612	0.3598	6.53	6.30	93.54	93.70
$C_{10}H_8$.	0.1031	0.0601	0.3542	6.52	....	93.70	....
	0.1024	0.0592	0.3511	6.47	....	93.51	....
Urea,	0.4022	0.2399	0.2960	6.67	6.70	20.07	19.96
$CO(NH_2)_2$.	0.4014	0.2454	0.2941	6.84	....	19.98	....
Glycocoll,	0.2528	0.1555	0.2972	6.88	6.71	32.06	31.96
$CH_2.NH_2.COOH$.	0.2053	0.1242	0.2412	6.77	....	32.04	....
Hippuric acid,	0.1733	0.0773	0.3829	4.99	5.06	60.26	60.30
$C_9H_9NO_3$.	0.1714	0.0767	0.3791	5.01	....	60.32	....
	0.1716	0.0782	0.3790	5.09	....	60.24	....
	0.1722	0.0794	0.3806	5.15	....	60.28	....
	0.1544	0.0691	0.3412	5.01	....	60.27	....
Uric acid,	0.2214	0.0485	0.2887	2.45	2.40	35.56	35.67
$C_5H_4N_4O_3$.	0.2506	0.0560	0.3266	2.50	....	35.54	....
Caffein, $C_8H_{10}N_4O_2$.	0.2026	0.0937	0.3668	5.18	5.19	49.38	49.42
Azobenzene,	0.1207	0.0609	0.3506	5.65	5.53	79.22	79.05
$(C_6H_5N)_2$.	0.1259	0.0622	0.3646	5.53	....	78.98	....

Table I (*Continued*).

Substance.	Weight taken. Gram.	Weight water found. Gram.	Weight carbon dioxide found. Gram.	Hydrogen. Found. Per cent.	Hydrogen. Theory. Per cent.	Carbon. Found. Per cent.	Carbon. Theory. Per cent.
Nitroguanidine, $NH_2.C:NH.NH.NO_2$.	0.2545	0.0898	0.1075	3.95	3.87	11.52	11.52
Dinitrobenzene, $C_6H_4(NO_2)_2$.	0.1555	0.0367	0.2445	2.64	2.40	42.88	42.83
	0.1563	0.0352	0.2456	2.52	....	42.86	....
	0.1564	0.0349	0.2457	2.50	....	42.85	....
	0.1521	0.0366	0.2390	2.68	....	42.85	....
Nitraniline, $C_6H_4.NO_2.NH_2$.	0.2055	0.0823	0.3935	4.48	4.38	52.22	52.13
	0.2023	0.0809	0.3876	4.47	....	52.25	....
Dinitraniline, $C_6H_3(NO_2)_2.NH_2$.	0.2277	0.0595	0.3295	2.92	2.75	39.46	39.32
	0.2046	0.0551	0.2936	3.01	....	39.14	....
Trinitrobenzene, $C_6H_3(NO_2)_3$.	0.2005	0.0361	0.2528	2.02	1.38	34.39	33.78
	0.2012	0.0318	0.2539	1.77	....	34.41	....
	0.2008	0.0315	0.2501	1.76	....	33.97	....
Trinitrophenol, $C_6H_2(NO_2)_3.OH$.	0.2903	0.0454	0.3346	1.75	1.32	31.44	31.42
Dinitronaphthol, $C_{10}H_5(NO_2)_2.OH$.	0.1957	0.0611	0.3708	3.49	2.58	51.67	51.25
	0.1500	0.0464	0.2827	3.46	....	51.40	....
Guanidine nitrate, $NH_2C:NH.NH_2,HNO_3$.	0.2150	0.1001	0.0845	5.21	4.95	10.72	9.82
Urea nitrate, $CO(NH_2)_2,HNO_3$.	0.2537	0.0985	0.0943	4.34	4.09	10.14	9.74

Atomic weights used: C = 12.001; H = 1.0075; N = 14.045; O = 16.00.

An examination of the results of the table shows that with the exception of the nitro bodies the percentages of hydrogen and carbon, as a rule, are near the theory. The inability to get perfectly pure oximes, azines, and glyoxyalines precluded experimenting with those compounds. The specimen of uric acid was found to contain 0.2 per cent of moisture and, if allowance be made for this, the percentages of hydrogen and carbon still more closely approach the theoretical.

In the case of dinitrobenzene the first discrepancy of any magnitude is observed. Here the percentage of hydrogen is invariably somewhat high, though the substance was found to be perfectly anhydrous.

Great difficulty was experienced in burning many of these compounds, as on heating they decomposed readily, and at times with explosive violence. It was found nearly impossible to obtain a regular combustion of picramide, picric acid, or dinitronaphthol. This latter compound, while relatively much less nitrated than either of the other two, gave off dense red fumes, completely filling the combustion tube. Guanidine and urea nitrates, though yielding large quantities of oxides of nitrogen, burned with great regularity.

While the oxides of nitrogen were, as a rule, wholly retained by the sulphuric acid in the water-absorbing tube a portion escaped into the carbon dioxide absorbers when trinitrobenzene, dinitronaphthol, guanidine nitrate, and urea nitrate were burned.

It thus appears that when burned as above described, compounds containing "unoxidized nitrogen" yield no oxides of nitrogen, at least none that is absorbed by sulphuric acid or soda-lime. Compounds containing the nitro group, on the other hand, do yield appreciable quantities of the oxides of nitrogen, which are absorbed in sulphuric acid and soda-lime. Nitraniline, though containing the nitro group, gave results differing but little from theory, and it is this fact that led to the method here described. Dinitrobenzene, when burned, yielded nitric oxide, while when one nitro group is reduced the resulting product, nitraniline, gave none. It appears, therefore, that when there is sufficient reducing material, such as carbon and hydrogen, in the molecule, and not too great a

proportion of nitro groups, the reducing material effects a reduction of the nitro group, and the nitrogen is then not reoxidized under the conditions of the combustion. Were a large number of combustions of nitrated bodies made, it would doubtless not be difficult to establish a relative proportion between the number of nitro groups and the carbon and hydrogen in the molecule necessary to effect the reduction of the oxides of nitrogen.

It is evident, however, that the nitric acid molecule existing in the two nitrates burned is not as readily reduced, for, while nitroguanidine gave theoretical results, the nitrate containing one more molecule of water yields large quantities of the oxides of nitrogen. Nitroguanidine therefore contains enough reducing material in its molecule to reduce completely the nitro group. The nitric acid molecule of the two nitrates is probably much more loosely combined and hence escapes reduction.

In the ordinary methods of combustion, it is customary to take some special precaution to eliminate any possible effect of the oxides of nitrogen on the final results. These precautions consist of one of two essentially different operations. In one case the oxides formed are absorbed by lead peroxide, manganese dioxide, potassium chromate, etc., or, more commonly, they are reduced by metallic copper and, in certain special methods, by metallic silver.

The absorption of the oxides is almost always adapted to special methods and is open to grave objections.

Gay-Lussac,[1] in 1815, used hot metallic copper turnings to reduce the oxides of nitrogen formed in the combustion of organic substances with cupric oxide, and this method is to-day almost universally used. As ordinarily described, a 10 centimeter length of cupric oxide is removed from the combustion tube and a reduced spiral of copper wire or a roll of copper gauze of the same length is inserted in the end of the combustion tube to which the absorbing train is connected. This operation is of itself time-consuming, but can be avoided if two combustion tubes are held prepared, one with the copper spiral and the other without it. Considerable difficulty

[1] Ann. d. chim., **95**, 184; **96**, 53.

has been experienced in satisfactorily reducing the copper spiral. If hydrogen is used, the gas must be specially purified and, as Neumann[1] has shown, copper obstinately retains material quantities of hydrogen which are later oxidized and weighed as water. Reduction by means of methyl or ethyl alcohol or formic acid has the advantage of being much quicker and less laborious than that in which hydrogen is used, but the copper retains the vapors of these bodies which are later oxidized, and materially increase the percentage of both hydrogen and carbon. It is often recommended to dry out the spiral in a current of hydrogen at a sufficiently high temperature to drive off the alcohol vapors, but in this operation considerable hydrogen is occluded. In drying out the spiral reduced by alcohol in a current of carbon dioxide, it has been found that enough carbon dioxide may be retained to vitiate the results. The reduced spirals are often dried in air though they are then rapidly coated with a superficial layer of copper oxide, and their efficiency thereby much impaired. The most satisfactory way is to allow the reduced spirals to remain a number of hours in a vacuum desiccator though, as is readily seen, this takes time, and a good vacuum desiccator is not always at hand.

A further objection to the use of copper spirals is the fact that, unless the air or oxygen is swept out of the combustion tube, the spiral becomes somewhat oxidized on heating. It is essential to replace the oxygen in the combustion tube with air, an operation requiring a gasometer or other supply of air.

The method here reported is the outcome of an attempt to secure a reduction of the copper with no danger of adding unknown amounts of carbon dioxide and water to the materials to be weighed. Those nitro compounds in whose molecule there is a deficiency of carbon and hydrogen are burned with an admixture of a known amount of a carbonaceous material of known composition. In this way the carbonaceous material including volatile gaseous products, and reduced copper, are all in the position to react with any oxides of nitrogen formed and effect their reduction.

The importance of pure materials cannot be overstated and

[1] Monatshefte, 13, 40.

for the purposes of this research, sucrose in the form of well-powdered rock-candy and Kahlbaum's pure benzoic acid, were found to be very satisfactory.

In many of the analyses sucrose was used, though the reducing material, the carbon (the hydrogen being theoretically at least all oxidized) is but 42 per cent of the weight of the substance. Benzoic acid and naphthalene are, weight for weight, much more active as reducing agents than sucrose. Nevertheless, in a large number of cases, the latter was used with excellent results.

Sucrose of a remarkable degree of purity and dryness may be obtained by pulverizing good crystals of rock candy after carefully removing the strings. This material is not very hygroscopic, and, unless the air is very moist, requires no further precaution for its preservation than to be placed in a well-stoppered bottle. In very damp weather, however, two hours' drying, after pulverization, in the water- or air-bath at not over 95°, will insure thorough dryness. All of the material used in connection with the analyses here given was not previously dried. As it was used in the analyses of sucrose given in Table I, it is seen to be chemically pure. The sucrose, owing to its purity, is always useful for check combustions to test the accuracy of the method of combustion.

In general, it has been found desirable to place the substance in the boat in such a manner as to leave a free space about a centimeter in length in the forward end. The greater portion of the sucrose, benzoic acid, or naphthalene is placed in this space and the remainder sprinkled over the top of the layer of substance. The end of the boat containing the sucrose is first inserted in the combustion tube, and the boat pushed in till it nearly touches the asbestos plug holding the layer of cupric oxide. The boat should not directly touch the cupric oxide but be separated by a centimeter layer of air. After heating the spiral in the anterior end of the tube, the heat is brought toward the boat from the middle of the combustion furnace; hence the cupric oxide becomes thoroughly heated before the end of the boat containing the reducing material is heated. The sucrose melts at 143° and distils towards 200°, giving off empyreumatic vapors which reduce a portion

of the contiguous cupric oxide, which becomes still more heated as the flames are turned on. The melted sucrose often mixes with or possibly partially dissolves the substance to be burned, and when the sucrose finally chars there is a large excess of carbon to aid in reducing the nitro group. Furthermore, the hot reduced copper may produce a decomposition of the gases with a deposition of finely divided carbon.

When benzoic acid is used, the greater portion of the acid is vaporized at a moderately low temperature, and no appreciable quantity of carbonaceous residue is left. In this case, therefore, the cupric oxide is reduced for a distance of several centimeters, but no carbon is left to aid in reducing oxides of nitrogen, save what may be formed on the hot reduced copper by the decomposition of the benzoic acid vapor, which passes over it. Hence it would appear that a carbonaceous residue in the boat is not essential to the reduction of the oxides of nitrogen.

When a new combustion tube is used, the presence of reduced copper is readily seen as a layer some 2 or 3 centimeters long in front of the boat, while the end of the rear cupric oxide spiral inserted after the boat is always seen to be partially reduced. Consequently there is a sufficient quantity of metallic copper to reduce thoroughly the maximum amount of oxides of nitrogen that can be formed.

Few nitro bodies are decomposed with an evolution of oxides of nitrogen below the temperatures necessary to secure the vaporization of benzoic acid or naphthalene or the dry distillation of sucrose. It may be necessary, however, in some cases to place the reducing material in a small copper boat a little ahead of the porcelain boat containing the material to be analyzed. In this case the copper could be reduced before the material was heated.

One gram of pure sucrose, when completely oxidized, yields 1.5430 grams of carbon dioxide and 0.5791 gram of water.

One gram of pure benzoic acid, when completely oxidized, yields 2.5235 grams of carbon dioxide and 0.4428 gram of water.

One gram of pure naphthalene, when completely oxidized,

yields 3.4357 grams of carbon dioxide and 0.5627 gram of water.

To determine the amount of carbon dioxide and water added by reason of the combustion of the sugar or benzoic acid or naphthalene, it is only necessary to multiply the weight of the material used in grams by the factors for carbon dioxide and water. The quantities of water and carbon dioxide calculated as being derived from the sucrose or benzoic acid used are then subtracted from the actual weights found and the resulting weights used as in the regular method of calculation.

Table II shows the results of analyses of various nitro bodies, using sucrose or benzoic acid to reduce the oxides of nitrogen formed :

The results given therein indicate what may be expected of the method, and it will be noticed that in all cases where discrepancies appear the quantity of water actually weighed is very small, and hence the error of weighing might, in many cases, cause a discrepancy no smaller than those obtained. The evidence, however, seems to indicate that no material, absorbed by the sulphuric acid or soda-lime, other than water and carbon dioxide, leaves the combustion tube.

Furthermore, as it is unnecessary to replace the oxygen left in the tube by air, the necessity of a second gasometer is obviated. Indeed, by this method one can make combustions of nitrogenous or non-nitrogenous bodies with no change in the manipulation other than the addition to the boat of a known weight of pure sucrose or benzoic acid.

While sucrose and benzoic acid are here recommended as reducing agents, many others may, of course, be used. Naphthalene suggests itself as the ideal substance, but it has been a matter of considerable difficulty to obtain perfectly pure naphthalene.

The explosive character of several of these compounds rendered combustion very difficult. It was found, however, that by mixing the finely powdered material with three or four volumes of pure, ground quartz the combustions proceeded with much greater regularity. Accordingly, many of the combustions above tabulated were made with an admixture of finely powdered silica. The silica contained no moisture and

Table II.

Material.	Weight taken. Gram.	Weight water found. Gram.	Weight carbon dioxide found. Gram.	Hydrogen. Found. Per cent.	Hydrogen. Theory. Per cent.	Carbon. Found. Per cent.	Carbon. Theory. Per cent.
Dinitrobenzene.							
Substance + sucrose	0.1959	0.0882	0.3049	....	....	....	....
Sucrose	0.1149	0.0665	0.1774	....	....	....	....
Substance	0.0810	0.0217	0.1275	2.38	2.40	42.93	42.83
Substance + sucrose	0.2057	0.0849	0.3200	....	....	....	....
Sucrose	0.1110	0.0643	0.1713	....	....	....	....
Substance	0.0947	0.0206	0.1487	2.43	2.40	42.82	42.83
Dinitrophenol.							
Substance + benzoic acid	0.2139	0.0566	0.3707	....	....	....	....
Benzoic acid	0.0595	0.0263	0.1502	....	....	....	....
Substance	0.1544	0.0303	0.2205	2.20	2.19	38.95	39.11
Substance + sucrose	0.2613	0.0963	0.3863	....	....	....	....
Sucrose	0.1137	0.0658	0.1754	....	....	....	....
Substance	0.1476	0.0305	0.2109	2.31	2.19	38.97	39.11
Trinitrobenzene.							
Substance + sucrose	0.2574	0.0813	0.3515	....	....	....	....
Sucrose	0.1069	0.0618	0.1650	....	....	....	....
Substance	0.1505	0.0195	0.1865	1.45	1.38	33.80	33.78

Table II (Continued).

Material.	Weight taken. Gram.	Weight water found. Gram.	Weight carbon dioxide found. Gram.	Hydrogen. Found. Per cent.	Hydrogen. Theory. Per cent.	Carbon. Found. Per cent.	Carbon. Theory. Per cent.
Substance + sucrose	0.2583	0.0809	0.3543	....	....	....	....
Sucrose	0.1053	0.0610	0.1625	....	....	....	....
Substance	0.1530	0.0199	0.1918	1.45	1.38	34.09	33.78
Substance + sucrose	0.2605	0.0832	0.3559	....	....	....	....
Sucrose	0.1084	0.0628	0.1673	....	....	....	....
Substance	0.1521	0.0204	0.1886	1.50	1.38	33.80	33.78
Substance + sucrose	0.2862	0.0931	0.3935	....	....	....	....
Sucrose	0.1295	0.0750	0.1998	....	....	....	....
Substance	0.1567	0.0181	0.1937	1.29	1.38	33.71	33.78
Substance + sucrose	0.2523	0.0789	0.3432	....	....	....	....
Sucrose	0.1017	0.0589	0.1570	....	....	....	....
Substance	0.1506	0.0200	0.1862	1.49	1.38	33.72	33.78
Trinitrophenol.							
Substance + benzoic acid	0.2130	0.0473	0.3306	....	....	....	....
Benzoic acid	0.0629	0.0279	0.1587	....	....	....	....
Substance	0.1501	0.0194	0.1719	1.45	1.32	31.24	31.42

Table II (*Continued*).

Material.	Weight taken.	Weight water found.	Weight carbon dioxide found.	Hydrogen.		Carbon.	
				Found.	Theory.	Found.	Theory.
	Gram.	Gram.	Gram.	Per cent.	Per cent.	Per cent.	Per cent.
Substance + benzoic acid	0.2297	0.0562	0.3833	....	....	....	....
Benzoic acid	0.0870	0.0385	0.2195	....	....	....	....
Substance	0.1427	0.0177	0.1638	1.39	1.32	31.31	31.42
Substance + benzoic acid	0.2207	0.0466	0.3373	....	....	....	....
Benzoic acid	0.0610	0.0270	0.1539	....	....	....	....
Substance	0.1597	0.0196	0.1834	1.37	1.32	31.32	31.42
Substance + benzoic acid	0.2151	0.0493	0.3454	....	....	....	....
Benzoic acid	0.0717	0.0317	0.1809	....	....	....	....
Substance	0.1434	0.0176	0.1645	1.38	1.32	31.29	31.42
Trinitraniline.							
Substance + benzoic acid	0.2498	0.0832	0.3269	....	....	....	....
Benzoic acid	0.0992	0.0574	0.1531	....	....	....	....
Substance	0.1506	0.0258	0.1738	1.92	1.77	31.48	31.55
Substance + benzoic acid	0.2256	0.0581	0.3652	....	....	....	....
Benzoic acid	0.0758	0.0336	0.1913	....	....	....	....
Substance	0.1498	0.0245	0.1739	1.79	1.77	31.66	31.55

Table II (Continued).

Material.	Weight taken. Gram.	Weight water found. Gram.	Weight carbon dioxide found. Gram.	Hydrogen. Found. Per cent.	Hydrogen. Theory. Per cent.	Carbon. Found. Per cent.	Carbon. Theory. Per cent.
Substance + benzoic acid	0.2125	0.0525	0.3314	....	....	....	....
Benzoic acid	0.0625	0.0277	0.1577	....	....	....	....
Substance	0.1500	0.0248	0.1737	1.85	1.77	31.58	31.55
Substance + benzoic acid	0.2042	0.0479	0.3125	....	....	....	....
Benzoic acid	0.0556	0.0246	0.1403	....	....	....	....
Substance	0.1486	0.0233	0.1722	1.75	1.77	31.60	31.55
Dinitronaphthol.							
Substance + benzoic acid	0.2109	0.0609	0.4321	....	....	....	....
Benzoic acid	0.0577	0.0255	0.1456	....	....	....	....
Substance	0.1532	0.0354	0.2865	2.55	2.58	51.00	51.25
Substance + benzoic acid	0.1750	0.0527	0.3611	....	....	....	....
Benzoic acid	0.0514	0.0228	0.1297	....	....	....	....
Substance	0.1236	0.0299	0.2314	2.71	2.58	51.06	51.25
Dinitraniline.							
Substance + benzoic acid	0.2094	0.0636	0.3659	....	....	....	....
Benzoic acid	0.0587	0.0260	0.1481	....	....	....	....
Substance	0.1507	0.0376	0.2178	2.79	2.75	39.41	39.32
Trinitrotoluol.							
Substance + benzoic acid	0.2197	0.0603	0.3733	....	....	....	....
Benzoic acid	0.0651	0.0288	0.1640	....	....	....	....
Substance	0.1546	0.0315	0.2093	2.28	2.22	36.92	36.98

Table II (Continued).

Material.	Weight taken. Gram.	Weight water found. Gram.	Weight carbon dioxide found. Gram.	Hydrogen. Found. Per cent.	Hydrogen. Theory. Per cent.	Carbon. Found. Per cent.	Carbon. Theory. Per cent.
Trinitroxylol.							
Substance + benzoic acid	0.1789	0.0572	0.3169	....	....	....	....
Benzoic acid	0.0530	0.0235	0.1337	....	....	....	....
Substance	0.1259	0.0337	0.1832	2.99	2.92	39.69	39.81
Substance + benzoic acid	0.1733	0.0544	0.3084	....	....	....	....
Benzoic acid	0.0528	0.0234	0.1332	....	....	....	....
Substance	0.1205	0.0310	0.1752	2.88	2.92	39.65	39.81
Urea nitrate.							
Substance + benzoic acid	0.3235	0.1236	0.2531	....	....	....	....
Benzoic acid	0.0640	0.0283	0.1615	....	....	....	....
Substance	0.2595	0.0953	0.0916	4.11	4.09	9.63	9.74
Substance + benzoic acid	0.3359	0.1290	0.2754	....	....	....	....
Benzoic acid	0.0720	0.0319	0.1817	....	....	....	....
Substance	0.2639	0.0971	0.0937	4.12	4.09	9.68	9.74
Guanidine nitrate.							
Substance + benzoic acid	0.3165	0.1408	0.2512	....	....	....	....
Benzoic acid	0.0627	0.0278	0.1582	....	....	....	....
Substance	0.2538	0.1130	0.0930	4.98	4.95	9.99	9.82
Substance + benzoic acid	0.3309	0.1455	0.2792	....	....	....	....
Benzoic acid	0.0741	0.0328	0.1870	....	....	....	....
Substance	0.2568	0.1127	0.0922	4.91	4.95	9.79	9.82

apparently exercised no injurious effect on the combustion of the material, for the percentages of carbon and hydrogen are in almost every case well within the limits of error when the quantity of material taken as well as its purity are considered. Furthermore, numerous combustions of sucrose and benzoic acid were made with a similar admixture of silica. In no case was any discrepancy in the analyses obtained. The residue remaining in the boat after the combustions was always perfectly white, indicating the absence of unoxidized material.

Singularly enough the admixture with silica has a direct influence on the reduction of the oxides of nitrogen and, though they are by no means completely reduced, they are present in the products of combustion in much smaller quantities.

Table III.

Substance.	Weight taken.	Weight water found.	Weight carbon dioxide found.	Hydrogen.		Carbon.	
				Found.	Theory.	Found.	Theory.
	Gram.	Gram.	Gram.	Per ct.	Per ct.	Per ct.	Per ct.
Trinitrobenzene	0.2069	0.0293	0.2580	1.58	1.38	34.01	33.78
Trinitrophenol	0.2893	0.0409	0.3340	1.58	1.32	31.49	31.42
	0.2791	0.0389	0.3228	1.56	...	31.54	....
	0.2838	0.0373	0.3277	1.47	...	31.49	....
Trinitraniline	0.2877	0.0469	0.3316	1.87	1.77	31.46	31.55
	0.2996	0.0502	0.3468	1.87	...	31.57	....

In Table III several combustions of highly nitrated bodies mixed with silica are given. It is seen that, while the percentages of hydrogen are still somewhat too high, the discrepancies are not as great as when the combustion is made of the material by itself, while the percentages of carbon are sufficiently accurate for most purposes.

The materials used in this investigation were for the most part of Kahlbaum's make, only those specimens showing widest variation from the theoretical being obtained elsewhere.

My thanks are due to Mr. Emil Osterberg, assistant in this laboratory, whose experimental skill has made the prosecution of this research possible.

The application of this method of reducing the oxides of nitrogen to the absolute determination of nitrogen, by the Dumas method, is to be investigated at an early date.

MIDDLETOWN, CONN.

Contribution from the Chemical Laboratory of the University of Utah.

AN APPARATUS FOR DETERMINING MOLECULAR WEIGHTS BY THE BOILING-POINT METHOD.

By Herbert N. McCoy.

The boiling-point method possesses two obvious natural advantages over the freezing-point method. In the former any solvent may be used, while the latter is restricted to a comparatively small number of solvents. At the boiling-point substances are, as a rule, much more soluble than at the freezing-point. Nevertheless, as a means of determining molecular weights, the freezing-point method has been very largely used in preference to the boiling-point method. This has been chiefly due to certain disadvantages attending the use of most forms of apparatus designed for boiling-point determinations.

The rather long time required to attain a constant boiling-point may lead to appreciable errors on account of intervening barometric changes. Further, the weight of the solvent placed in the boiling vessel does not represent the true weight that is effective in forming the solution, as a fraction, indefinite in amount, always exists in the state of vapor. In most forms of apparatus the cold liquid, formed by the condensation of this vapor, constantly drops back into the boiling liquid, hindering greatly the establishment of equilibrium. However, this latter disturbing influence is largely eliminated in the forms of apparatus devised by Hite[1] and Jones.[2]

The main difficulty has lain in obtaining regular boiling without superheating. Numerous devices, such as glass beads, garnets, balls of platinum gauze, and a platinum wire, sealed into the glass, have been used, as is well known, to avoid this difficulty. While it is true that these have been more or less successful in accomplishing the desired end, at the same time they have complicated the apparatus and made the working of the methods more troublesome.

A distinct innovation was introduced by Sakurai,[3] who

[1] This Journal, **17**, 514.
[2] *Ibid.*, **19**, 58.
[3] J. Chem. Soc., **61**, 993.

prevented superheating and produced regular boiling by passing the vapor of the pure solvent into the liquid whose boiling-point was to be measured, external heat being also applied.

Following up this advance, Landsberger has described a method[1] by which many of the difficulties of the older boiling-point methods have been overcome. The apparatus is simple. The process is very rapid, and the results are fully as good as those obtained by means of the elaborate apparatus of Beckmann.[2]

According to Landsberger's method a state of equilibrium between the liquid and vapor phases is quickly attained by substituting for the direct source of heat usually employed to raise the liquid to its boiling-point, the latent heat of the vapor of the pure solvent. The liquid whose boiling-point is to be determined according to Landsberger's method is contained in a large test-tube, holding also the thermometer, and surrounded also by a larger tube which serves as a jacket. The vapor is generated in a flask by direct heat and is conducted into the liquid in the inner tube, rapidly bringing it to its boiling-point. A hole in the side of the inner test-tube near the cork allows the excess of vapor to pass into the jacket and a side neck of the latter leads the uncondensed portion of the vapor from the jacket to an ordinary condenser.

That a solution, even a saturated one, may be heated to its boiling-point by the vapor of the pure solvent, has long been known. It is obvious, however, that no superheating can occur as the liquid and vapor can exist in contact at but one definite temperature. No beads or garnets, etc., are required. Thorough mixing of the liquid and vapor is insured. No cold liquid runs back into the boiling vessel and radiation is largely prevented by the jacket which is filled with hot vapor. Since a determination can be made in half an hour, barometric changes have little effect on the results.

Walker and Lumsden[3] have improved Landsberger's apparatus by using a graduated inner tube and measuring the volume of the solution instead of weighing it; a procedure

[1] Ber. d. chem. Ges., **31**, 458.
[2] Ztschr. phys. Chem., **8**, 226.
[3] J. Chem. Soc., **73**, 502.

which Beckmann[1] has shown to be equally applicable. The graduated tube allows a determination of the real volume of the solution. This is preferable to a knowledge of the whole amount of solvent present, part of which necessarily exists as vapor at the time the boiling-point is measured, thus rendering the solution more concentrated than the amount of solvent weighed out would indicate. Of greater importance is the fact that several determinations of the molecular weight may be made with the same quantity of substance, by observing the boiling-point at different dilutions, the corresponding volumes being read off on the graduated tube.

In the method just described the jacket must be kept filled with vapor at the temperature of the boiling-point of the solvent. To do this requires a more rapid current of vapor passing through the solution than would otherwise be necessary to establish equilibrium between vapor and the solution. Now, as the solution is heated solely by the latent heat of this vapor, there is with some solvents, notably benzene, a rapid condensation of the vapor in the inner tube. The condensation is greater the smaller the ratio of the latent heat to the specific heat of the solvent employed. The dilution thus caused soon increases the volume of the solution beyond the capacity of the apparatus and so limits the number of duplicate determinations to one or two.

In applying Walker and Lumsden's modification of Landsberger's method, it occurred to me that the difficulty just mentioned would be remedied and other advantages would be gained by combining the functions of the boiling-flask and the jacket. As a result the apparatus shown in the figure has been devised.[2]

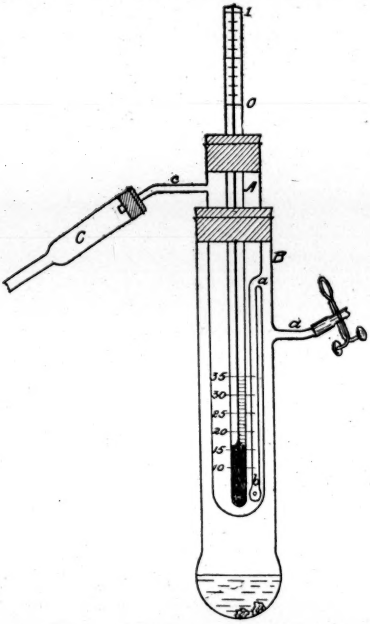
The vessels *A* and *B* are of glass. The smaller one, *A*, in which the thermometer is placed, is 20 cm. long and 2.7 cm. wide. Its lower portion is graduated between the points marking 10 cc. and 35 cc. It has a narrow tube *ab*, opening to the exterior at *a*, 7.5 cm. from the open end. The tube *ab* is closed at the lower end *b* and perforated with five small holes. Another tube, *c*, 2.5 cm. from the mouth of *A*, leads to a Liebig's condenser *C*. The jacket *B* is 22 cm. long and

[1] Ztschr. phys. Chem., 6, 472.

[2] This apparatus may be obtained from Eimer & Amend, New York.

4 cm. wide, excepting near the bottom where it is somewhat enlarged. A short tube *d*, bent upward slightly, is attached to the jacket about 7 cm. from the mouth. The tube *d* is closed by a rubber tube and Mohr's pinch-clamp. A is held in position by a cork fitting tightly into the jacket.

When a determination is to be made the apparatus is sup-



ported by a universal clamp and the tube *c* is connected with a Liebig's condenser. About 50 cc. of the pure solvent and a small piece of clay tile are placed in the jacket and 12–16 cc. of the solvent in the inner tube. The liquid in the jacket is heated to boiling by a small flame, best protected from air currents by a small iron chimney, such as is used in analytical work. The bit of tile promotes regular boiling and the vapor

heats the liquid in the graduated tube nearly to its boiling-point by contact with the outside of the inner tube. But as soon as the liquid in the graduated tube has become hot, the vapor rises in the jacket and forces its way through the tube *ab* into the liquid in the graduated tube and brings it to its boiling-point. Before this point is reached the liquid in the jacket may be allowed to boil briskly, but now the heat is to be adjusted so that the liquid in the inner tube boils slowly but regularly, and a very slow distillation into the condenser takes place.

When the thermometer is constant, or does not change more than 0.001 of 1° in thirty seconds, the reading is taken as the boiling-point of the pure solvent. This point is reached, as a rule, in from five to ten minutes after the heating is commenced. The pinch-clamp closing the tube *d* is now removed and then the flame is withdrawn. If the flame be withdrawn before admitting air through *d* the liquid in the inner tube runs over into the jacket through the tube *ab*.

The weighed substance, whose molecular weight is to be determined, is now introduced by raising the stopper carrying the thermometer, *d* is closed, and the solvent in the jacket again boiled. If the substance dissolves readily, the solution quickly reaches its boiling-point and the thermometer reading becomes constant in a very short time. Usually only three or four minutes elapse between the time of reading the boiling point of the solvent and that of the solution. After the boiling-point of the solution is taken the tube *d* is again opened and the boiling stopped. The volume of the solution is read at once, after lifting the thermometer out of the solution.

To obtain further readings at greater dilution, the thermometer is replaced and a new determination of the boiling-point made. The corresponding volume is read off as before. In this way five, six, or even more determinations of the boiling-point may be made with the same amount of substance. Since, at each heating, some of the solvent will condense in the inner tube, the volume of the solution will be a little greater at each successive reading and the boiling-point of the solution will decrease accordingly. The volume that condenses in the graduated tube at each heating is small. It is

greatest with benzene, where it amounts to only 2.5 cc. With water the increase was but a few tenths of a cubic centimeter, so that a little water was added each time in order to increase the dilution by larger increments.

The molecular weight is calculated from the formula

$$M = \frac{W \cdot T}{\Delta \cdot V},$$

where W is the weight of the substance, Δ the elevation of the boiling-point, and V the volume of the solution. T is a constant having a different value for each solvent. This formula is very similar to that used when the weight of the solvent instead of the volume of the solution is determined, the only difference being the replacement of the factor representing the weight by that indicating the volume. The values of T in the above formula are obtained from the corresponding values for the old formula by dividing the latter by the specific gravity of the solvent at its boiling-point.

The following are the values of T for a few common solvents :[1]

Alcohol	1560	Carbon bisulphide	1940
Ether	3030	Acetone	2220
Chloroform	2600	Aniline	3820
Benzene	3280	Water	540

The apparatus has been tested by determining the molecular weight of a number of substances, using four different solvents. The results have been very satisfactory. No tedious and troublesome precautions seem to be necessary to obtain fairly good results and the time required is very much less than is needed for a determination with the Beckmann apparatus. Frequently the apparatus has been set up, the substance weighed out, and a determination made at two dilutions in less than thirty minutes.

In the determinations here recorded the weighings were made on a simple balance, sensitive to milligrams, and the Beckmann differential thermometer was read by means of a hand lens. The substances whose molecular weights were determined were the so-called chemically pure preparations of

[1] Beckmann : Ztschr. phys. Chem., 6, 472.

C. A. F. Kahlbaum not further purified. The alcohol used was Kahlbaum's absolute, treated with anhydrous copper sulphate. The benzene was Kahlbaum's thiophene-free preparation, made from benzoic acid. It was dried with metallic sodium. The ether was of good quality. It was washed many times with water, dried with calcium chloride, and distilled over metallic sodium. The determinations were not made with the object of attaining the greatest possible accuracy, but rather to test the value of the apparatus for practical use in ordinary organic research. In the last column the values found by Beckmann, at about the same concentration, are given for comparison.

SOLVENT, ALCOHOL; T = 1560.

Naphthalene, 128.

Weight of substance.	Volume of solution.	Elevation of boiling-point.	Molecular weight found.	Beckmann found.
0.806	28.0	0.291	154	155
"	29.0	0.278	156	

Benzoic Acid, 122.

1.010	24.2	0.535	122	124
"	25.3	0.519	120	

Salicylic Acid, 138.

0.995	24.1	0.452	142	140
"	25.3	0.435	141	

Benzanilid, 197.

0.626	15.2	0.299	215
"	17.9	0.262	208

SOLVENT, BENZENE; T = 3280.

Benzil, 210.

Weight of substance.	Volume of solution.	Elevation of boiling-point.	Molecular weight found.	Beckmann found.
0.950	19.3	0.670	241	230
"	21.8	0.570	250	236

Salicylic Acid, 138.

0.985	22.5	0.549	261	234
1.000	24.0	0.538	256	

Naphthalene, 128.

0.981	19.1	1.301	130	144
"	21.6	1.141	131	

SOLVENT, ETHER; T = 3030.

Naphthalene, 128.

Weight of substance.	Volume of solution.	Elevation of boiling-point.	Molecular weight found.	Beckmann found.
1.025	16.0	1.498	130	132

SOLVENT, WATER; T = 540.

Boric Acid, 62.

Weight of substance.	Volume of solution.	Elevation of boiling-point.	Molecular weight found.	Beckmann found.
1.015	27.3	0.309	65.0	66.8
"	28.6	0.297	64.5	
"	31.1	0.282	62.5	
"	33.4	0.262	62.6	
"	36.0	0.247	61.7	
1.030	29.0	0.297	64.5	

Urea, 60.

1.203	18.2	0.542	66.2	73
"	21.2	0.465	66.3	
"	23.1	0.439	64.4	
"	25.4	0.396	64.9	
"	28.0	0.358	65.2	
"	30.4	0.343	62.7	
"	35.0	0.293	63.7	72

Mannite, 180.

2.044	18.8	0.294	199	
"	22.8	0.254	190	192
"	25.8	0.233	183	
"	30.5	0.200	181	

SALT LAKE CITY, Jan. 29, 1900.

REVIEWS.

ELEMENTARY CHEMISTRY. FOR HIGH SCHOOLS AND ACADEMIES. By ALBERT L. AREY, C.E., Rochester, New York, High School. New York: Macmillan & Co. London: Macmillan & Co. 1899.

The thought that has guided the author in the preparation of this book is expressed in his own words, thus: "It was decided to omit all reference to those properties of the substances studied in the laboratory, which can be learned by observation of the substances themselves; to render the work more complete than it would otherwise be by stating such properties as cannot be shown by experiments adapted to secondary schools." This assumes that the pupil at the outset is capable of making good observations. This does not accord with experience. It is the object of a laboratory course to train these powers of observation. It would certainly be interesting to read the note-books of pupils who, without directions from the teacher, should record the results of their first observations on chemical substances. Of course, the pupil should be led to use his own eyes and his own mind as much as possible, but it is only with the aid of a thoroughly conscientious teacher, who sees the needs of the pupil, that this power can be developed.

On page 4 an extremely dangerous experiment is described, thus: "Sulfur and potassium chlorate are mixed in a mortar with considerable friction." What the results would be of attempts by inexperienced persons to perform this experiment the writer of this notice shudders to think. Not a word of caution is given. It is all very well to say that this is an experiment to be performed by the instructor, but many instructors in chemistry have had very little experience, and they are as likely to go astray as the average pupil.

On page 5 are found directions for an experiment which is not clear, though it sounds learned. The pupil is directed to weigh a quantity of sulphuric acid and a solution of calcium chloride; then to pour them together and weigh the two vessels again. The pupil is then asked: "Does chemical action change the total quantity of matter in existence? Was the total quantity of sulphuric acid in the world increased or diminished by the above experiment? How was the total quantity of calcium chloride affected?" As a matter of fact, the total quantity of sulphuric acid in the world is diminished by such an experiment, but the pupil cannot possibly know this unless told. In the next question the pupil is asked to state his opinion as to why solution aids chemical action. If

the pupil ventures to express an opinion at this stage of his work he ought to be reprimanded very promptly.

Instances of this kind are frequent throughout the book and are characteristic of it. They show clearly that the writer of the book is not a well-trained chemist. He may be an excellent teacher, but he has not shown that he is by the book that he has written; and this book, in the hands of inexperienced teachers, would not be helpful. An experienced teacher, on the other hand, might detect these defects, but it would be necessary for him to be on the alert at every stage. I. R.

VICTOR VON RICHTER'S ORGANIC CHEMISTRY, OR CHEMISTRY OF THE CARBON COMPOUNDS. Edited by PROF. R. ANSCHÜTZ, University of Bonn (Assisted by DR. G. SCHROETTER). Authorized translation by EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania. Third American from the Eighth German Edition. Volume II. Carbocyclic and Heterocyclic Series. Philadelphia: P. Blakiston's Son & Co., 1012 Walnut St. 1900. pp. 671+xvi. Price, $3.00.

Last year attention was called to the first volume of this book that had then just been published. Now we have presented the "aromatic" and related compounds, or the "carbocyclic and heterocyclic series." The book has been so long known and so favorably known that comments upon it are superfluous. The work of editing and of translating has been in most competent hands, so that we may be sure that no pains have been spared to bring it up-to-date in every respect. As remarked in the earlier notice, it is not adapted to the use of the beginner, who would surely be drowned if he should plunge in or even wade in too far. It is a shorter book of reference, a good thing to have on the study table, whether the table belongs to a student or a teacher. It is not, of course, a substitute for Beilstein—nothing could play that part successfully—but still it will be found helpful in many cases if Beilstein is lacking or if completeness is not aimed at. It is condensed to an extent rarely met with, and to such an extent as to make it hard to follow in places. Take, for example, the treatment of the "Constitution of the Benzene Nucleus," which covers not quite two pages of small type. All that is said is no doubt correct, but either the reader must understand the subject beforehand, or his efforts to find out what this means will surely end in a bad headache. It may, however, serve a useful purpose as a reminder to the old stager. I. R.